Photocatalytic Activities of Metal Oxide Semiconductors for Oxygen Isotope Exchange and Oxidation Reactions

INTRODUCTION

Powdered metal oxide semiconductors have been widely used as photocatalysts of the oxidation of organic and inorganic compounds (*1*), the decomposition of inorganic compounds (*1*), and various photoelectrochemical reactions (when metallized) (*2*). Photocatalytic activities of semiconductors depend strongly on their preparation methods. The factors influencing the photocatalytic activity, however, have not been well understood. With this connection Courbon *et al.* (*3*) have reported that oxygen isotope exchange between $^{18}O_2$ and the oxygen in TiO_2 (gas–solid oxygen isotope exchange, GSOIE) occurs under band-gap illumination, and that the photocatalytic activity of TiO_2 for GSOIE correlates well with that for the photooxidation of isobutane. We have also found a good correlation between both the photocatalytic activities for GSOIE and for the photooxidation of C_2H_6 over titanium hydroxide calcined at various temperatures (*4*). These results could give a promising clue to better understanding of a mechanism of photocatalytic process over metal oxide semiconductors and the factors governing the photocatalytic activity.

In the present study we have measured the photocatalytic activities of various oxide semiconductors for GSOIE, oxygen isotope equilibration between $^{18}O_2$ and $^{16}O_2$ (GOIE), and the oxidation of CO and C_2H_6 with O_2 and to examine the activity correlation among them. On the basis of the results, the mechanism of the photocatalytic OIE and oxidation reactions as well as the factors influencing the photocatalytic activity were discussed.

EXPERIMENTAL

Semiconductors used were TiO_2 (anatase and rutile), $SrTiO_3$, $BaTiO_3$, ZnO, In_2O_3, ZrO_2, Fe_2O_3, and WO_3, which were supplied from various companies. For TiO_2 the photocatalytic activity of the samples from different sources was compared. The surface area of these semiconductors was measured by the BET method after outgasing at room temperature. $^{18}O_2$ (99 at.%) was obtained from Prochem.

The reactions were carried out at room temperature in a closed circulation system evacuable to 10^{-7} Torr (1 Torr = 133.3 N m^{-2}). The sample of 0.1–0.3 g was spread on the flat bottom of a quartz reaction cell and outgased at 200°C for 1 hr. The light source was a 500-W high-pressure Hg lamp (Ushio, UIV-570) that was filtered through a band pass (Toshiba UV-D33S, 240–400 nm) and a water filter to remove heat. A mirror was used to illuminate the sample from the top. Reaction products were sampled at appropriate intervals and analyzed with a mass spectrometer.

For GSOIE neat $^{18}O_2$ was used and for GOIE $^{18}O_2$ was mixed with $^{16}O_2$ in the ratio 1 : 3. For photooxidation reactions, CO and O_2 were mixed in the ratio 2 : 1, and C_2H_6 and O_2 in the ratio 1 : 2. The pressure of O_2 in all the reactions was adjusted to 1–2 Torr.

Since isotope exchange reactions obey first-order kinetics irrespective of a reaction mechanism (*5*), the photocatalytic activity for GIOE was evaluated with first-order rate constant. In the present experiments the GOIE reaction was so fast over most samples that its rate could not be mea-

295

sured accurately under a full output of illumination, and therefore, the intensity of light was reduced with a 5% neutral density filter in the activity measurements for GOIE. The rates thus measured were then converted into the values under the full illumination. Although GSOIE also obeys first-order kinetics, its rate constant was not determined because the ^{18}O concentration in dioxygen at equilibrium was unknown. The photocatalytic activity for GSOIE was evaluated with the amount (μmole) of total ^{16}O (i.e., $^{16}O_2 + \frac{1}{2}{}^{16}O^{18}O$) appeared in the gas phase during 1 hr of illumination.

Since the photooxidation of CO and C_2H_6 with O_2 was found to obey first-order kinetics with respect to O_2 pressure under the present experimental conditions, the photocatalytic activity for the photooxidation reactions was evaluated with first-order rate constant.

RESULTS

Anatase has been often used as a photocatalyst, and it is well known that its photocatalytic activity depends strongly on the preparation method (1). In the present ex-

FIG. 1. First-order plots of dioxygen isotope equilibration, $^{18}O_2 + {}^{16}O_2 \rightleftharpoons 2{}^{18}O^{16}O$ (GOIE) over TiO_2 (Merck, anatase), where x is the fraction of $^{18}O^{16}O$ and the suffix 0 or e denotes the value of x at $t = 0$ or at equilibrium. The plots show that the reaction is accelerated with illumination time.

periment commercial anatase showed much different activity from sample to sample in all the test reactions as shown in Table 1, and even the samples from different manufacturing lots from the same company did not exhibit the same activity.

In the GOIE reaction an induction period was observed on some samples, i.e., the reaction was accelerated with illumination time as shown in Fig. 1. To our knowledge such behavior of GOIE has not been reported before. Since steady state rates were not observed before equilibrium in any cases where the acceleration occurred, the maximum rate constants observed are listed in Table 1. The induction period of the GOIE reaction was still observed in the subsequent run carried out after evacuating the gases used in the preceding run, suggesting that the acceleration was not due to catalyst activation which is sometimes observed in thermal catalytic reactions. The acceleration of GOIE was, however, not investigated further. GOIE was so much faster than GSOIE that the activity measurement for the former was not disturbed by the latter.

In photoelectrochemical (PEC) reactions

TABLE I

Photocatalytic Activities of TiO_2 (Anatase) for Gas–Solid Oxygen Isotope Exchange between $^{18}O_2$ and TiO_2 (GSOIE), Dioxygen Isotope Equilibration (GOIE), and the Photooxidation of CO and $C_2H_6{}^a$

Source	Surface area (m²/g)	Oxygen isotope exchange		Photo-oxidation	
		GSOIE	GOIE	CO	C_2H_6
Aerosil P-25[b]	40	2.2	148	1.1	6.4
Fuji titanium TP-2	17	0.94	60	0.80	3.6
Merck	12	0.12	>260[c]	0.32	0.33
Merck (reduced)[d]	12	0.16	>52[c]	0.10	0.40
Kanto	12	0.53	>320[c]	0.38	3.6
MCB	11	0.72	152	0.34	3.0
MCB[e]	8	<0.03	0	0	0.01

[a] The activity for GSOIE was evaluated with the amount (μmole) of total ^{16}O ($^{16}O_2 + \frac{1}{2}{}^{18}O^{16}O$) formed during 1 hr of illumination, and the other activities were evaluated with the first-order rate constants of relevant reactions.
[b] Identical with Degussa P-25.
[c] Maximum rate observed (see text).
[d] Reduced in H_2 at 600°C for 6 hr.
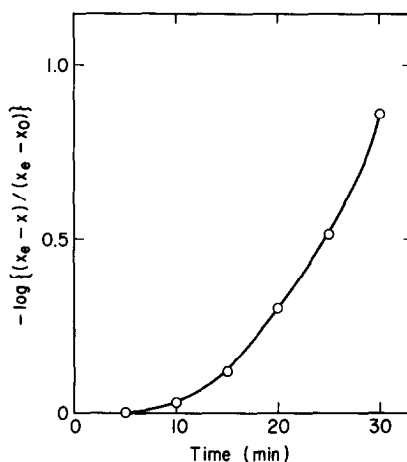[e] A small amount of rutile is included.

such as a photoassisted water–gas shift reaction over platinized TiO_2 (6), the photocatalytic activity is enhanced by the reduction of TiO_2 in H_2 at high temperatures (6, 7). In this connection the photocatalytic activity of reduced TiO_2 (Merck) was measured in the present experiment. As seen in Table 1 the reduced sample is not as active in the test reactions as in PEC reactions. This result indicates that PEC reactions are different in mechanism from photooxidation reactions. In PEC reactions cathodic sites, which are usually metal deposited on a semiconductor, are apart from anodic sites so that the electronic conductivity of the semiconductor should be low to transfer photogenerated electrons through the bulk of semiconductor, while in photooxidation and OIE reactions the electron mobility is not so important since these reactions can be completed on the sites close to each other.

The products of C_2H_6 photooxidation were CO_2 and H_2O, and any other products could not be detected in the gas phase.

Table 2 shows that the photocatalytic activities of commercial rutile are lower than standard anatase and less dependent on the variety of its source. The samples from Aldrich are different in purity and the one

TABLE 2

Photocatalytic Activities of TiO_2 (Rutile) for Gas–Solid Oxygen Isotope Exchange between $^{18}O_2$ and TiO_2 (GSOIE), Dioxygen Isotope Equilibration (GOIE), and the Photooxidation of CO and C_2H_6 [a]

Source	Surface area (m^2/g)	Oxygen isotope exchange		Photo-oxidation	
		GSOIE	GOIE	CO	C_2H_6
Aldrich[b]	2.4	0.59	>11[c]	0.4	0.97
Aldrich[d]	1.6	<0.03	26	0.17	0.41
Furuuchi	2.7	0.37	18	0.46	0.78
Kishida	2.4	0.32	15	0.45	0.76
Katayama	4.6	0.18	15	0.36	1.1

[a] The activity for GSOIE was evaluated with the amount (μmole) of total ^{16}O ($^{16}O_2$ + $\frac{1}{2}^{18}O^{16}O$) formed during 1 hr of illumination, and the other activities were evaluated with the first-order rate constants of relevant reactions.
[b] 99.9%.
[c] Maximum rate observed.
[d] 99.99%.

TABLE 3

Photocatalytic Activities of other Metal Oxide Semiconductors for Gas–Solid Oxygen Isotope Exchange between $^{18}O_2$ and Semiconductors (GSOIE), Dioxygen Isotope Equilibration (GOIE), and the Photooxidation of CO and C_2H_6 [a]

Semi-conductor	Source	Oxygen isotope exchange		Photo-oxidation	
		GSOIE	GOIE	CO	C_2H_6
$SrTiO_3$	Furuuchi	0.31	60	0.2	0.69
	Alfa	0.04	0.4	0.03	0.06
$BaTiO_3$	Kanto	—	—	0	0
ZnO	Kadox 25	0.73	0.08	0.83	1.1
	Yamanaka	0.18	>0.1	1.6	2.3
In_2O_3	Nakarai	0.22	0.3	0	0.06
ZrO_2	Kanto	1.1	10	0.08	0.06
WO_3	Yamanaka	0	0	0	0
Fe_2O_3	Yamanaka	0	0	0	0

[a] The activity for GSOIE was evaluated with the amount (μmole) of total ^{16}O ($^{16}O_2$ + $\frac{1}{2}^{18}O^{16}O$) formed during 1 hr of illumination, and the other activities were evaluated with the first-order rate constants of relevant reactions.

with lower purity showed higher activity in the test reactions except for GOIE. It should, however, be noted that the high-purity rutile has less surface area than others.
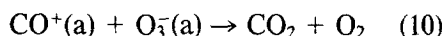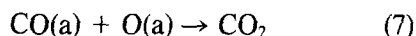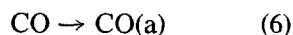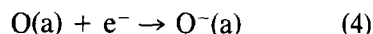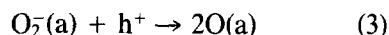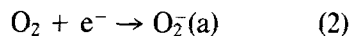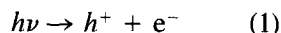
Table 3 shows the photocatalytic activities of other popular semiconductors of metal oxide in which band-gap energy ranges from 2.2 to 5.0 eV. The band-gap energy of ZrO_2 is too high (5.0 eV) to absorb the light used in the present experiment, but the diffuse reflection spectrum of the ZrO_2 sample showed a little absorption at around 320 nm. The photocatalytic activity of the ZrO_2 sample may be due to this absorption band which probably arises from the impurity level. The activities of $SrTiO_3$ and ZnO depended on their source. The $SrTiO_3$ sample from Alfa showed almost no activity when it was used as supplied, but it became somewhat active after being calcined at 400°C in O_2. This is probably due to an impurity because the Alfa $SrTiO_3$ sample was found to contain much sulfur oxide. The impurity in semiconductor photocatalysts exerts a great influence on photocatalytic activity since it often functions as a recombination center of pho-

togenerated electron and hole. The In_2O_3 sample showed very low activity, while the sample prepared from indium hydroxide exhibited higher activity than a commercial one (8). Fe_2O_3 and WO_3 showed no activity even when these semiconductors were prepared from hydroxides. Inactivity of some semiconductors may be due to a poor charge separation of the electron–hole pair.

DISCUSSION

Figure 2 summarizes the results obtained for TiO_2 (from Tables 1 and 2), in which the activities for GSOIE and CO photooxidation are plotted against the activity for CO photooxidation. We can see from Fig. 2 that these activities correlate with each other although the relationship has some scattering and seems nonlinear. It is reasonable that there is a good correlation among the photocatalytic activities for oxidation reactions, because the reaction mechanism is probably similar. Although there are some variations of the proposed

mechanism for photooxidation reactions over oxide semiconductors (1), possible reaction schemes involved in CO photooxidation could be summarized as follows:

$$h\nu \to h^+ + e^- \tag{1}$$

$$O_2 + e^- \to O_2^-(a) \tag{2}$$

$$O_2^-(a) + h^+ \to 2O(a) \tag{3}$$

$$O(a) + e^- \to O^-(a) \tag{4}$$

$$O^-(a) + O_2 \to O_3^-(a) \tag{5}$$

$$CO \to CO(a) \tag{6}$$

$$CO(a) + O(a) \to CO_2 \tag{7}$$

$$CO(a) + h^+ \to CO^+(a) \tag{8}$$

$$CO^+(a) + O^-(a) \to CO_2 \tag{9}$$

$$CO^+(a) + O_3^-(a) \to CO_2 + O_2 \tag{10}$$

On TiO_2 O^- or O_3^- has not been observed by ESR but very recently O_3^- was observed by Anpo et al. (9). The photooxidation of alkane also proceeds by a similar mechanism in which dissociated oxygen species and the lattice oxygen of semiconductor are involved (1). In any photooxidation reactions the dissociation of dioxygen is believed to be rate-limiting, and especially O^- (or O_3^-) is considered to be the most important species because ESR experiments have shown its high reactivity with oxidizable materials. In addition, activated dioxygen in a singlet state, which is also formed over illuminated oxide semiconductors (10, 11), may play an important role in photooxidation reactions.

The present experiments showed that the decreasing rate of oxygen in C_2H_6 photooxidation is much faster than in CO photooxidation. This result could be explained in terms of the thermal autoxidation of partially oxidized products in the former reaction. Alkane is photooxidized via alcohol and aldehyde eventually to CO_2 and H_2O (12), and some partially oxidized products may be so reactive as to react directly with dioxygen without band-gap light.

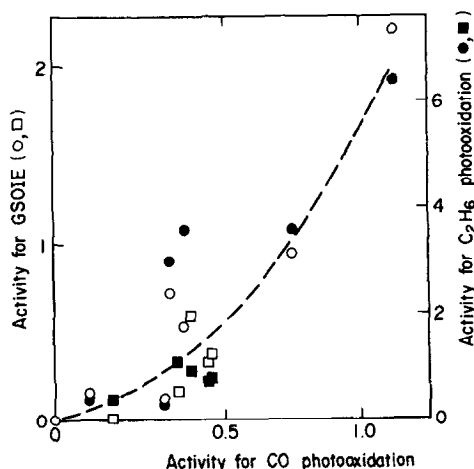The mechanism of GSOIE has not yet been established. In the previous paper (4)

FIG. 2. Photocatalytic activities of TiO_2 (anatase and rutile) for gas–solid oxygen isotope exchange between $^{18}O_2$ and TiO_2 (GSOIE) and C_2H_6 oxidation as a function of the photocatalytic activity for CO oxidation (from Tables 1 and 2). ○, ●, anatase; □, ■, rutile. The activity for GSOIE was evaluated with the amount (μmole) of total ^{18}O formed during 1 hr of illumination, and the oxidation activities were evaluated with the first-order rate constants of relevant reactions.

we described that the lattice oxygen of TiO_2 is exchangeable with dioxygen under band-gap illumination. In our recent experiments, however, we found that over-illuminated TiO_2 (P-25) dioxygen was readily exchanged with the surface hydroxyls which oxygen had been exchanged with ^{18}O of $H_2^{18}O$ at room temperature and that GSOIE was significantly suppressed when the hydroxyls were modified with Si oxides while photooxidation reactions were not so affected (13). These results indicate that the hydroxyl groups of TiO_2 mainly participate in GSOIE. In addition, the presence of CO or hydrocarbon completely retards GSOIE (3, 4), suggesting that GSOIE has the same oxygen intermediate as in photooxidation reactions. The correlation between the photocatalytic activities for GSOIE and photooxidation reactions also suggests that the rate-determining process is the same in both of the reactions.

The above conclusions on the photoactivity correlation of TiO_2 could be applicable to the other oxide semiconductors.

The photocatalytic activity of oxide semiconductors for GOIE, however, has almost no correlation with the other photocatalytic activities as seen from Tables 1–3, though the proposed mechanism of GOIE also involves O_2^- (14). If GOIE involves the same rate-limiting step as in photooxidation reactions, then some correlation between the photocatalytic activities for GOIE and oxidation reactions could be expected. GOIE is also different from other oxygen isotope exchange reactions such as GSOIE in that the acceleration of reaction rate is often observed in GOIE. These results suggest that GOIE may occur without O^- or O_2^-, but further speculation is not warranted at present.

The results of Tables 1 and 2 show that the photocatalytic activities of TiO_2 for GSOIE and oxidation reactions correlates well with the surface area, i.e., the larger the surface area, the higher the activity. Although such a surface-area dependence is quite reasonable in thermal catalysis be-

cause all the surface of a catalyst equally participates in a thermal catalytic reaction, it seems to us that this relation is not a self-evident fact in photocatalysis, because only illuminated surface can participate in a photocatalytic reaction and its area would not be proportional to the total surface area of photocatalyst as far as the penetration of incident light into the photocatalyst due to reflection is not so significant. Therefore, we assume that the density of active sites on oxide semiconductors increases with an increase in surface area. Such active sites are probably related to lattice defects, edge or grain boundary, since these could increase with an increase in surface area (i.e., with a decrease in particle size) and function as a hole-trapping center which may enhance the charge separation of eletron–hole pair.

In summary, the photocatalytic activity of powdered oxide semiconductor depends upon crystal structure, impurity, and surface states (lattice defect, dangling bond, etc.) of semiconductor, which would be related to the efficiency of charge separation (recombination) as well as to the thermal catalytic activity for gas adsorption.

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