# Photocatalytic Hydrogenation of Alkynes and Alkenes with Water over TiO<sub>2</sub>. Pt-Loading **Effect on the Primary Processes**

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Photoreactions of alkynes and alkenes with water have been investigated over Pt-loaded and unloaded TiO<sub>2</sub> in order to obtain information about the effects of Pt loading on photocatalytic reactions. With unloaded TiO2, the major photoformed products are those formed by the hydrogenation accompanied by the fission of the C=C or C=C bond of the reactants, while with Pt-loaded TiO<sub>2</sub>, i.e., Pt/TiO<sub>2</sub>, a significant enhancement of hydrogenation reaction without the bond fission is observed. In addition to those products, oxidation products such as CO and  $CO_2$  are found. In contrast to the features with unloaded TiO<sub>2</sub>, with Pt/TiO<sub>2</sub> there is no marked difference between the yields of the oxidation and reduction products. ESR measurements show that photoformed electrons are accumulated as localized  $Ti^{3+}$  ions with unloaded  $TiO_2$ , whereas with  $Pt/TiO_2$  electrons are easily transferred from  $TiO_2$  to Pt particles. From these results and those of kinetic studies the significance of the close existence of electrons and holes for unloaded TiO<sub>2</sub> proposed in the preceding paper is confirmed. Furthermore, it has been shown that with  $Pt/TiO_2$  a photoelectrochemical process is predominant, the reduction of H<sup>+</sup> on Pt particles and the oxidation by OH on TiO<sub>2</sub> bringing about photohydrogenation without bond fission and formation of oxidation products, respectively.

#### Introduction

As an approach to the utilization of solar energy, photocatalytic decomposition of water into  $H_2$  and  $O_2$  over various metal oxides has recently received a great deal of attention.<sup>1</sup> In connection with this problem, it has been established that the photocatalytic activity of metal oxides such as TiO<sub>2</sub>, SrTiO<sub>3</sub>, etc. for the decomposition of water and its reaction with alcohol is enhanced markedly by the addition of small amounts of Pt, Pd, or  $RuO_{2}$ .<sup>1</sup> Such enhancement in the activity has been explained by the concept that the photoformed electrons are transferred from the oxides to the loaded metal particles, resulting in a decrease in electron-hole recombination. There seems to be many papers concerning this problem, but there is little direct evidence supporting such electron transfer in gas-phase photocatalytic reactions.

Recently, we have reported that charge transfer excited complexes,  $[Me^{(n-1)+}-O^-]^*$ , with close photoformed electrons and holes, are important for the fission of the C=C bond of alkenes resulting in photoinduced metathesis reactions over MoO<sub>3</sub> supported on porous Vycor glass.<sup>2</sup> Furthermore in the preceding paper, it has also been shown that such close electrons and holes play a significant role in the photohydrogenation of alkynes and alkenes when accompanied by fission of the C=C or C=C bond of the reactants over TiO<sub>2</sub>-containing adsorbed water.<sup>3</sup>

The study of the effect of Pt loading on those photohydrogenations appears to provide information about the validity of the mechanism proposed for the reactions over unloaded TiO<sub>2</sub> as well as the differences between the mechanisms for the reactions over Pt-loaded and unloaded TiO<sub>2</sub>. Somorjai and Wagner<sup>4</sup> and Hall and Van Damme<sup>5</sup> have proposed that the photodecomposition of water proceeds by a photoelectrochemical mechanism over

TABLE I: Yields of the Photoformed Products from C<sub>3</sub>H<sub>4</sub> over TiO<sub>2</sub> at 300 K<sup>a</sup>

catalysts	Pt content, wt %	products, $10^{-9}$ mol m <sup>-2</sup> h <sup>-1</sup>						
type		$\overline{CH_4}$	$C_2H_6$	$C_2H_4$	$C_3H_6$	$C_3H_8$	$C_3/C_2^d$	
P-25 <sup>b</sup> P-25 <sup>b</sup> P-25 <sup>c</sup> Rutile <sup>b</sup>	0 0.4 4.0 4.0 0	1.90 2.10 2.40 1.70 0.55	12.3 13.7 15.7 11.1 3.27	0.40 0.54 0.50 0.60 0.10	1.10 4.04 15.7 0.73 0.48	0.50 0.35 0.40 0.64 0.19	0.12 0.27 0.86 0.10 0.17	
P-25 <sup>b</sup> P-25 <sup>c</sup> Rutile <sup>b</sup> Rutile <sup>b</sup>	4.0 4.0 0 4.0	2.40 1.70 0.55 0.22	15.7 11.1 3.27 1.60	0.50 0.60 0.10 0.23	15.7 0.73 0.48 10.3	0.40 0.64 0.19 1.10	0. 0. 0. 5.	

<sup>a</sup> The adsorption of H<sub>2</sub>O vapor at 18 torr at 300 K was followed by degassing at the same temperature. The pressure of  $C_3H_4$  was 5.0 torr. <sup>b</sup> $H_2$  reduction was carried out at 473 K. <sup>c</sup> $H_2$  reduction was carried out at 773 K.  ${}^{d}C_{3}/C_{2} = (C_{3}H_{6} + C_{3}H_{8})/(CH_{4} + C_{2}H_{4} + C_{2}H_{6})$ . BET surface area: P-25, 40 m<sup>2</sup>/g; rutile 7.5 m<sup>2</sup>/g. Average particle size: P-25, 290 Å; rutile, 2000–1000 Å.

Pt-loaded oxides and by a photocatalytic mechanism over unloaded oxides. In the former the oxidation and reduction reactions take place on different sites of the catalyst, while in the latter both reactions occur on sites very close to each other. Ther are few studies concerning the difference in reaction mechanisms betweem Pt-loaded and unloaded TiO<sub>2</sub>.<sup>1a,b,4,5</sup> This problem seems to be important for a complete understanding of the photocatalysis of metal oxides.

## **Experimental Section**

Materials. Two kinds of TiO<sub>2</sub> were used. One is P-25, Degussa (obtained from the Japan Aerosil Co.), consisting of 80% anatase and 20% rutile. The other is pure rutile from Ishihara Industry Co. Their surface area and average particle sizes are shown in Table I. The reactant gases as well as  $H_2$  were of extrapure grade from the Takachiho Co. They were used without further purification. Commercial tank oxygen was purified by low-temperature distillation. Deionized double-distilled water was degassed by alternate freezing and thawing in vacuo.

Apparatus and Procedure. Details of the apparatus and procedure were described in the preceding paper.<sup>3</sup> Pt-loaded TiO<sub>2</sub> catalysts  $(Pt/TiO_2)$  were prepared by mixing of the desired amounts of TiO2 and platinum black powder followed by sufficient grinding in an agate mortar. Reduction of the catalysts was carried out with  $H_2$  in the following two manners: In one case, the catalysts were subjected to reduction at 773 K for 1 h followed by evacuation at 723 K for 0.5 h, while in the other case they were subjected to reduction at 473 K for 2 h followed by evacuation at the same temperature. In both cases, evacuation after the reduction was continued during the temperature decrease to room

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TABLE II: Yields of the Photoformed Products from  $C_3H_4$  over TiO<sub>2</sub> at 300 K<sup>a</sup>

Pt content, wt %	products, $10^{-9}$ mol m <sup>-2</sup> h <sup>-1</sup>									
	CO <sub>2</sub>	CO	CH4	$C_2H_4$	$C_2H_6$	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> /C <sub>2</sub>		
0 4.0	22.7 37.2	4.38 8.14	1.27 1.63	0.24 0.43	3.55 2.92	0.867 19.2	0.135 2.87	0.20 4.42		
quantum yield, % <sup>b</sup>	0.51		0.021		0.039	0.29	<b>0.04</b> 1			

<sup>a</sup>TiO<sub>2</sub> (P-25) was reduced by H<sub>2</sub> at 473 K. The pressure of H<sub>2</sub>O was 17.0 torr. <sup>b</sup>Quantum yields were measured at  $350 \pm 10$  nm over Pt/TiO<sub>2</sub>. Quantum yields = nnumber of photoformed products)/ (number of irradiated photons).



Figure 1. Time course of the photohydrogenation reaction of  $CH_3C \equiv CH$  with water over Pt-loaded TiO<sub>2</sub> at 300 K (Pt content, 4 wt %; UV-29 filter, cut  $\lambda < 290$  nm).

temperature. The reaction temperature was kept at 300 K with a water bath, and the reactant gas was introduced into the reaction cell. Then the UV irradiation was carried out with a 75-W Hg lamp with color and water filters (290 nm <  $\lambda$  < 500 nm). The reaction products was sampled at various times and analyzed by a gas chromatograph. The quantum yield for the reactions was determined by using a monochromator equipped with a 500-W Xe lamp. The number of incident photons to the cell was determined by potassium ferrioxalate actimometry. ESR measurements were carried out at 77 K with a JES-ME-1X (X-band).  $Mn^{2+}$  ions in MgO powder were used for g value and sweep calibration. The UV irradiation for ESR measurements was carried out by using a 500-W high-pressure mercury lamp with a color filter ( $\lambda > 290$  nm) in a ESR cavity. To determine the particle size of the catalysts, X-rays diffraction and transmission electron microscopy were applied.

### **Results and Discussion**

Products of Photocatalytic Reactions over Pt-Loaded and Unloaded  $TiO_2$ . Tables I and II show the products of the photoreaction of CH<sub>3</sub>C=CH and their yields over Pt-loaded and unloaded TiO<sub>2</sub>. The relative amounts of water and  $CH_3C \equiv CH$ in Table I are different from those in Table II. With unloaded TiO<sub>2</sub>, the major products arise from hydrogenation accompanied by the fission of the C=C bond (hereafter called photohydrogenolysis), in agreement with the results in the preceding paper.<sup>3</sup> On the other hand, with Pt-loaded  $TiO_2$  the yields of the products of hydrogenation without the C=C bond fission ( $C_3H_6$ ,  $C_{1}H_{2}$  (hereafter called photohydrogenation) increases markedly, its extent being larger with a higher Pt content. Simultaneously, the yields of the photohydrogenolysis products scarecely change, a slight decrease being observed with rutile. Such features are reflected in the change of the  $C_3/C_2$  values caused by Pt loading. Similar results were obtained with other reactants such as  $CH_2 = CH_2$ ,  $CH_3 CH = CH_2$ , CH = CH, etc. Table I also shows little or no effect of Pt loading for  $Pt/TiO_2$  reduced with  $H_2$  at 773 K, i.e., the SMSI behavior observed in the photoreaction over TiO<sub>2</sub>.6



Figure 2. Time course of the photohydrogenation reaction of  $CH_3C \equiv CH$  in the absence of water over Pt-loaded TiO<sub>2</sub> (Pt content, 4 wt %).



Figure 3. Growth of the ESR signal of the photoformed  $Ti^{3+}$  ions over Pt-loaded and unloaded  $TiO_2$  at 77 K.

As shown in Figure 1, in the presence of water vapor at 1.6 torr, on UV irradiation of Pt/TiO2 the photoreaction takes place immediately, its yield increasing linearly with irradiation time. On the other hand, when no water vapor or adsorbed water are present, the photoreaction is initiated by UV irradiation, but its rate decreases, leveling off after 5 h (Figure 2). The total amount of the products formed prior to the cessation of the reaction (6.6  $\times$  10<sup>-6</sup> mol/0.24 g of catalyst) was approximately equal to that of water desorbed from the catalyst up to 373 K (7.7  $\times$  10<sup>-6</sup> mol/0.24 g of catalyst) which has been determined in a separate experiment. The total amount of water desorbed up to 873 K was  $22.1 \times 10^{-6}$  mol/0.24 g of catalyst. From the results, it is concluded that weakly adsorbed molecular water plays a significant role in photoreactions over Pt/TiO2. Similar behavior has been observed with the photodecomposition of water over Pt-loaded oxides.1c

Table II also shows the yields of oxidation products such as CO and CO<sub>2</sub> together with the quantum yields of all the products. With unloaded TiO<sub>2</sub>, the yields of the oxidation products are much higher than those of the photohydrogenation products.<sup>3</sup> With Pt-loaded TiO<sub>2</sub>, there is no marked difference between both yields. This suggests that photoreactions over Pt-loaded TiO<sub>2</sub> are much more catalytic in nature as compared to those over unloaded TiO<sub>2</sub>.<sup>5</sup>

Electron Transfer from  $TiO_2$  to Pt Particles. In order to clarify the nature of such a difference in the feature of the photoreactions over Pt-loaded and unloaded TiO<sub>2</sub>, the following ESR measurements were carried out with both catalysts in the presence of water and CH<sub>3</sub>C=CH, i.e., under same conditions as those for the photoreactions. As seen in Figure 3, with unloaded TiO<sub>2</sub>, the ESR signal attributable to Ti<sup>3+</sup> ions appears, its intensity increasing linearly with irradiation time. With Pt/TiO<sub>2</sub>, little or no change

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Figure 4. Effect of the pressure of water on the yields of photoformed products from  $CH_3CH=CH_2$  over Pt-loaded TiO<sub>2</sub> (Pt content, 4 wt %;  $CH_3CH=CH_2$ , 3.0 torr; TiO<sub>2</sub>, P-25).

in the ESR signal due to  $Ti^{3+}$  ions is observed. As has been shown in the work of Ward and Bard,<sup>7</sup> the reactivity of photoformed holes on TiO<sub>2</sub> is much higher than that of photoformed electrons, i.e.,  $Ti^{3+}$  ions, resulting in the accumulation of electrons on TiO<sub>2</sub>, i.e., the increase in the intensity of the ESR signal due to  $Ti^{3+}$  ions. This suggests that with Pt/TiO<sub>2</sub> photoformed electrons will be transferred from TiO<sub>2</sub> to Pt particles.

The causes of such electron transfer have been discussed by a number of workers.<sup>1,7,8</sup> It is not attributable to the formation of the Schottky barrier, since th contact between Pt and TiO<sub>2</sub> has been shown to be ohmic.<sup>8,9</sup> It appears most likely that enhancement of the reaction  $H^+ + e^- \rightarrow \dot{H}$  by the catalytic effect of Pt brings about such electron transfer.<sup>1,7,8,10</sup>

According to the work of White et al., the SMSI behavior observed with  $Pt/TiO_2$  is attributable to the occurrence of electron transfer from  $TiO_2$  to Pt particles.<sup>6b</sup> In the case where such electron tansfer occurs, the electrons which had already transferred to Pt particles would retard further transfer of photoformed electrons from  $TiO_2$  to Pt. Such explanations are in agreement with the results shown in the present work.

Difference in the Reaction Mechanisms between Pt-Loaded and Unloaded TiO<sub>2</sub>. From the considerations described above, it is concluded that a marked increase in the yields of photohydrogenation products arises from the addition reaction of H atom to alkenes or alkynes which proceeds on the Pt particles. The H atoms are formed by the reaction  $H^+ + e^- \rightarrow H$ , where the electrons are transferred from TiO<sub>2</sub>. On the other hand, according to the model proposed in the preceding paper,<sup>3</sup> the photohydrogenolysis reactions proceed via the interaction of alkynes (or alkenes) with the electron-hole pair formed on TiO<sub>2</sub>. Accordingly, the photohydrogenation and photohydrogenolysis reactions proceed on different parts of the Pt/TiO<sub>2</sub> and by different mechanisms.

This conclusion is supported by the difference in the character of both reactions. Figure 4 shows the change of the yields of the photoreaction products with H<sub>2</sub>O pressure over Pt/TiO<sub>2</sub>. With increasing H<sub>2</sub>O pressure the yields of the photohydrogenolysis products (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) decrease, while the yields of the photohydrogenation product (C<sub>3</sub>H<sub>8</sub>) increase. Such a decrease in the yields of CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub> with increasing H<sub>2</sub>O pressure has also been observed with the photoreaction of CH<sub>3</sub>C=CH over unloaded TiO<sub>2</sub>. As seen in Figure 5, there is little or no change in the rates of photoreactions of various alkenes over Pt/TiO<sub>2</sub>, while the



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Figure 5. Relationship between the ionization potential of reactants and the rates of their photoreactions over Pt-loaded and unloaded TiO<sub>2</sub> at 300 K (a, CH<sub>2</sub>=CH<sub>2</sub>; b, CH<sub>3</sub>CH=CH<sub>2</sub>; c, *i*-C<sub>4</sub>H<sub>8</sub>; d, 1,3-C<sub>4</sub>H<sub>6</sub>).

corresponding values for unloaded TiO<sub>2</sub> increase with lowering of the ionization potential of alkenes. Such a feature would be explicable as follows: The presence of water vapor will interfere with the interaction of the electron-hole pair with alkenes which is important in the photohydrogenolysis reactions.<sup>11</sup> Such interaction is expected to be stronger with an alkene having a lower ionization potential. Thus, the photohydrogenolysis will be retarded by water vapor, its rate varying from one alkene to another. On the other hand, the photohydrogenation reaction requires no such interaction, resulting in similar rates of reaction throughout all alkenes and also in the lack of a retarding effect for water. The rate increases with increasing pressure of water might be attributed to an efficient supply of  $H^+$  from donation of  $H_2O$ . Thus, the following reaction mechanisms are proposed for the photohydrogenolysis and photohydrogenation reactions of alkynes (or alkenes) with water over Pt-loaded and unloaded TiO<sub>2</sub>. unloaded TiO<sub>2</sub>

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Pt/TiO2

$$HO_2$$
 - e + n  
- + H<sup>+</sup> - + (on Pt) hydrogenation reaction  
+ + OH<sup>-</sup> - OH (on TiO<sub>2</sub>) oxidation reaction

According to the work of Bard and Ward,<sup>7b</sup> with small semiconductor particles (<2000 Å) the thickness of the space charge layer is not sufficient to separate photoformed excitons to free electrons and holes. The electron and hole pair such as  $Ti^{3+}$  and O<sup>-</sup> play a significant role in photocatalytic reactions. This suggests that in the present work charge separation is more efficient for rutile (2000–1000 Å) than for P-25 (200–300 Å). Such a difference between catalysts might explain the larger value of C<sub>3</sub>/C<sub>2</sub> as well as the marked effect of Pt loading observed with rutile.

**Registry No.**  $CH_2$ — $CH_2$ , 74-85-1;  $CH_3CH$ — $CH_2$ , 115-07-1; CH= CH, 74-86-2; 1,3-C<sub>4</sub>H<sub>6</sub>, 106-99-0; *i*-C<sub>4</sub>H<sub>8</sub>, 115-11-7; CH<sub>3</sub>C=CH, 74-99-7; Pt, 7440-06-4; TiO<sub>2</sub>, 13463-67-7.

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