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The Photocatalytic Activity of a Platinized Titanium Dioxide Catalyst Supported over Silica

Kazunari Domen, Yoshihisa Sakata, Akihiko Kudo, Ken-ichi Maruya, and Takaharu Onishi*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227
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The effect of the amount of TiO_2 loading on the photocatalytic activity of H_2 evolution from aqueous methanol solution over a platinized TiO_2/SiO_2 catalyst was studied. UV diffuse reflectance spectra of TiO_2/SiO_2 showed the blue shift of absorption edge for the catalyst of lower amount of TiO_2 loading, which suggested the higher dispersion of TiO_2 on SiO_2. The activity decreased monotonously with the decrease of the amount of TiO_2 loading over SiO_2, i.e. with the increase of the dispersion.

Various photo-induced reactions over TiO_2 powder have been studied by many workers. For example the photo-oxidation of hydrocarbons by O_2,[1,2] photo-adsorption and desorption of O_2,[3–5] and hydrogenation of unsaturated hydrocarbons[6,7] were reported. On the other hand, the platinized TiO_2 powder is known as an effective photocatalyst for some reactions, such as photo-Kolbe reaction[8,9] and the H_2 evolution from aqueous solutions containing organic compounds.[10,11] In the latter system, the catalyst is generally regarded as a micro-photoelectrochemical cell. In that model, both the electron in the conduction band and the hole in the valence band are produced by the band gap irradiation, and then the excited electron reduces a reactant over the platinum surface, and the hole oxidizes a reactant over the TiO_2 surface. Therefore the electron and the hole have to be separated and to migrate to those reaction sites. On such "charge-separation" type reactions, the effects of the particle size[12,13] and also the crystal structures of TiO_2 (anatase, rutile, or amorphous)[14,15] upon the photocatalytic activities were reported.

Recently Anpo et al. studied the photocatalytic activities of hydrogenation of unsaturated hydrocarbons with H_2O over titanium-silicon oxides[16] and titanium oxide anchored onto porous Vycol glass.[17] They concluded that the high dispersion of titanium oxide resulted in the high activity for the reaction. In their system, localized electron-hole pair excited by photon seems to be an active species. For the "charge-separation" type reaction, however, the effect of the loading of the photoactive materials over an insulator with a large surface area has been scarcely studied.[18,19] In this paper, the activity of platinized TiO_2 supported over SiO_2 for the H_2 evolution from aqueous methanol solution is reported.

Experimental

A titanium sulfate solution (24.0% as $Ti(SO_4)_2$) was purchased from Kanto Chemical Co. and hexachloroplatinic acid was obtained from Wako Pure Chemical Ind. SiO_2 with ca. 200 $m^2 g^{-1}$ of BET surface area (Degussa) was used. A TiO_2/SiO_2 catalyst was prepared by an impregnation method: SiO_2 powder impregnated with aqueous titanium sulfate solution was stirred for 1 h and then it was dried by a rotary evaporator, followed by calcination at various temperatures for 2 h in air.

The reaction was carried out using a closed gas circulation system (ca. 300 ml) attached with a vacuum line. A reaction vessel (200 ml) made of Pyrex glass was irradiated through a flat window. An aqueous methanol solution suspended with the catalyst was stirred magnetically. The measurement of the activity of the H_2 evolution was carried out as follows. The aqueous methanol solution (typically 100 ml of methanol and 100 ml of water) containing TiO_2/SiO_2 and H_2PtCl_6 was degassed until no air peaks were detected in the gas phase by gas chromatography. Then, the solution was irradiated by an Xe lamp (USHIO, UXL 500D-O, 500 W), which was used at 300 W for obtaining a stable intensity of light for a long time. The amount of evolved H_2 was measured by gas chromatography (MS 5A column, Ar carrier) attached directly to the closed circulation system.

Catalysts were characterized using X-ray diffraction (Rigaku), X-ray photoelectron spectroscopy (Shimadzu, ESCA-750) and UV diffuse reflectance spectroscopy (JASCO UVIDEC-505). The surface area of the catalyst was determined by BET measurement. The quantum yield at 365 nm was measured using a monochrometer (H. 20, ISA JOBIN YVON Instrument) and thermopile (The Eppley Laboratory Inc.)

Results and Discussion

Characterization of TiO_2/SiO_2 Calcined at Various Temperatures. SiO_2 impregnated with aqueous $Ti(SO_4)_2$ solution was dried and calcined at various temperatures. Titanium sulfate began to decompose at about 673 K. In Table 1, the BET surface areas and

Table 1. BET Surface Areas and Ratios of XPS Peak Area of TiO_2(5 wt%)/SiO_2 Calcined at Various Temperatures

Calcination temperature	BET surface area	Ratio of peak area	
K	$m^2 \cdot g^{-1}$	Ti/Si	O/Si
673	126	0.61	0.73
833	170	0.61	0.70
998	180	0.56	0.70
1073	170	0.55	0.72

The surface area of SiO_2 used in the experimental was 202 $m^2 \cdot g^{-1}$.

the results of XPS of TiO_2(5 wt%)/SiO_2 calcined at various temperatures are shown. The surfase area increased with the increase of calcination temperature from 673 K to 833 K and it was almost constant above 833 K. Sulfur was observed on the sample calcined at 673 K by XPS, while no sulfur remained on those calcined above 998 K.

The signal intensity ratio of Ti(2p3/2)/Si(2s), decreased ca. 10% at high calcination temperatures (998 K and 1073 K), probably due to the sintering of supported TiO_2, which resulted in the decrease of the surface area. In the X-ray diffraction (XRD) pattern, no clear peak of TiO_2 was observed in TiO_2 (5 wt%)/SiO_2 at any calcination temperatures.

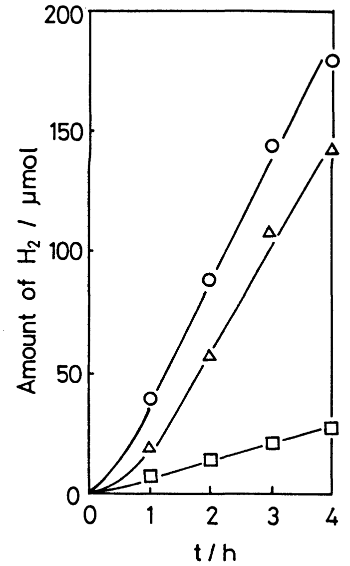

Fig. 1. H_2 evolution from aqueous methanol solution (50 vol%) over Pt-TiO_2/SiO_2 catalysts. ○: Pt(1 wt%)-TiO_2(2 wt%)/SiO_2, △: Pt(0.5 wt%)-TiO_2(2 wt%)/SiO_2, □: Pt(0.1 wt%)-TiO_2(2 wt%)/SiO_2, catalyst: 0.5 g, solution: 200 ml, an Xe lamp (500 W) was used at 300 W.

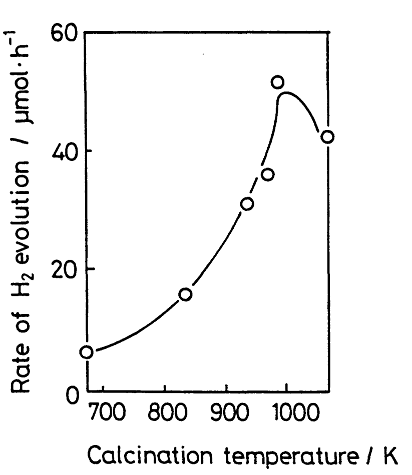

Fig. 2. Dependence of the rate of H_2 evolution from aqueous methanol solution (50 vol%) over Pt-(1 wt%)-TiO_2(5 wt%)/SiO_2 upon the calcination temperature for TiO_2/SiO_2. Catalyst: 0.5 g, solution: 200 ml.

Dependence of the Activity upon the Calcination Temperature of TiO_2/SiO_2. Typical H_2 evolution behaviours are shown in Fig. 1. The rate of the H_2 evolution was a little slower at the beginning than that at the steady state, probably due to the reduction of platinum. Therefore, the rate of the H_2 evolution at the steady state was regarded as the activity of the catalyst.

The dependence of the activity of the Pt (1 wt%)-TiO_2 (5 wt%)/SiO_2 catalyst upon the calcination temperature of TiO_2/SiO_2 is shown in Fig. 2. Pt (1 wt%)-TiO_2 (5 wt%)/SiO_2 denotes the catalyst which contains 1 wt% of Pt against TiO_2, and 5 wt% of TiO_2 against SiO_2. The activity increased markedly with the increase of the calcination temperature up to 998 K, and decreased slightly at higher temperature. Thus, in this study all the catalysts were calcined at 998 K.

UV Diffuse Reflectance Spectra of TiO_2/SiO_2. In Fig. 3, UV diffuse reflectance spectra of TiO_2/SiO_2 samples calcined at 998 K are shown. With the decrease of the amount of TiO_2, the absorption edge shifted monotonously to shorter wavelength. Similar blue shifts were previously reported in TiO_2/SiO_2 mixed oxide[16] and TiO_2 anchored on porous Vycor glass.[17] This phenomenon is interpreted by the so-called quantization effect,[20,21] which arises from the confinement of charge carriers in a semiconductor of a small volume. Thus, the blue shift of absorption spectra shown in Fig. 3 could be attributed to the change of the dispersion of supported TiO_2 on SiO_2, i.e. for the lower loading of TiO_2, higher dispersion

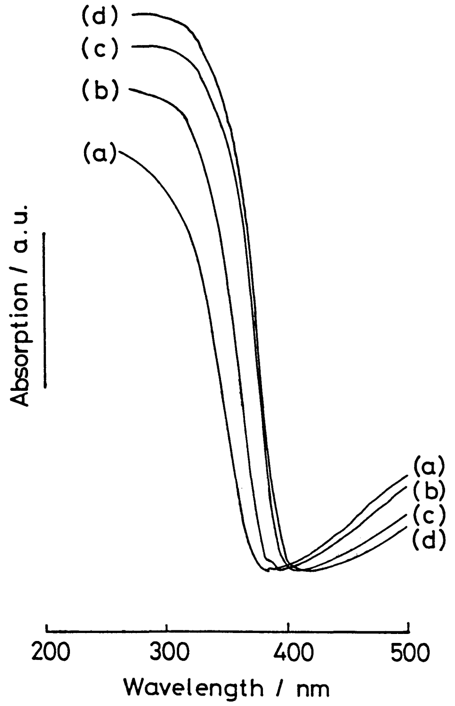

Fig. 3. UV diffuse reflectance spectra of various TiO_2/SiO_2 catalysts calcined at 998 K. (a); TiO_2(0.5 wt%)/SiO_2, (b); TiO_2(2 wt%)/SiO_2, (c); TiO_2(10 wt%)/SiO_2 (d); TiO_2(20 wt%)/SiO_2.

was achieved and, electrons and holes were confined in a smaller volume of TiO_2. Thus, it is concluded that TiO_2 is supported on SiO_2 and that the degree of the dispersion is controlled by changing the amount of the loading of TiO_2.

Dependence of the Activity upon the Amount of Pt Supported on TiO_2/SiO_2. The dependence of the activities upon the amounts of supported Pt over several kinds of TiO_2/SiO_2 catalysts are shown in Fig. 4. The activities increased in proportion to the amounts of supported platinum in the region of small platinum loading on TiO_2. This may suggest that most part of Pt, added as H_2PtCl_6, was reduced and worked as the catalyst for the H_2 evolution on TiO_2. In the higher loading region, the activities decreased gradually with the increases of the amounts of platinum. Since the color of the catalyst changed from gray to dark gray or black with the increase of Pt loading, one of the reasons for the decrease of the activity is due to the decrease of the amount of photons absorbed in TiO_2 because of the absorption of UV photons by Pt metal particles. Another one is the increase of the possibility of the recombination of an electron and a hole over platinum.

The optimum amount of Pt was different in each catalyst, as shown in Fig. 4. With the decrease of the amount of supported TiO_2 over SiO_2, the optimum ratio of Pt to TiO_2 increased.

Comparison of the Intrinsic Photocatalytic Activities of the H_2 Evolution among Pt-TiO_2/SiO_2 Catalysts. To compare the intrinsic photocatalytic activities, the amount of Pt loading was fixed at the value which each catalyst showed the maximum activity as indicated in Fig. 4. Figure 5 depicts the dependence of the rates of the H_2 evolution upon the amounts of catalysts in aqueous methanol solution. For all catalysts, the activity increased with the increase of the amount of the catalyst and reached the value which was almost independent of the amount of the catalyst. Under the condition of the saturated amount of catalyst, almost all photons, which had larger energy than the band gap of TiO_2 and entered into the reaction vessel, should be absorbed by TiO_2 although a small part of photons might go out by scattering. Therefore, the rate at the saturated amount of the catalyst was regarded as the intrinsic activity for the Pt-TiO_2/SiO_2 catalyst, which was normalized by the number of the absorbed photons. It should be noted that the number of the absorbed photons is different in each catalyst, because the UV absorption edge shifted to the shorter wavelength region with the decrease of TiO_2 loading as shown in Fig. 3. It was estimated that TiO_2 (0.5 wt%)/SiO_2 absorbed by about 30% smaller number of photons than TiO_2 (20 wt%)/SiO_2 did. On the other hand, the activity of TiO_2 (20 wt%)/SiO_2 was higher by ca. 3 times than that of TiO_2 (0.5 wt%)/SiO_2 under the same irradiation condition as shown in Fig. 5.

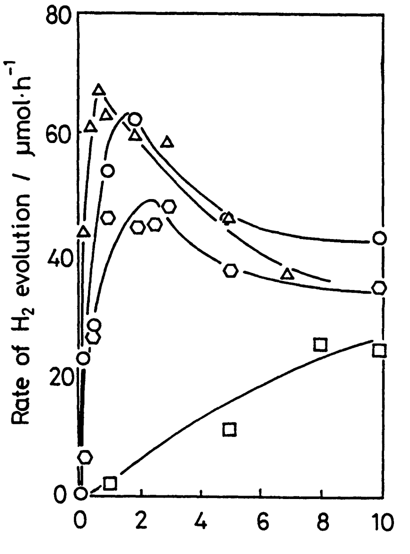

Fig. 4. Dependence of the rates of H_2 evolution from aqueous methanol solution (50 vol%) over various TiO_2/SiO_2 catalysts calcined at 998 K upon the amounts of loaded platinum. □: TiO_2(0.5 wt%)/SiO_2, ○: TiO_2(2 wt%)/SiO_2, ○: TiO_2-(5 wt%)/SiO_2, △: TiO_2(10 wt%)/SiO_2, catalyst: 0.5 g, solution: 200 ml.

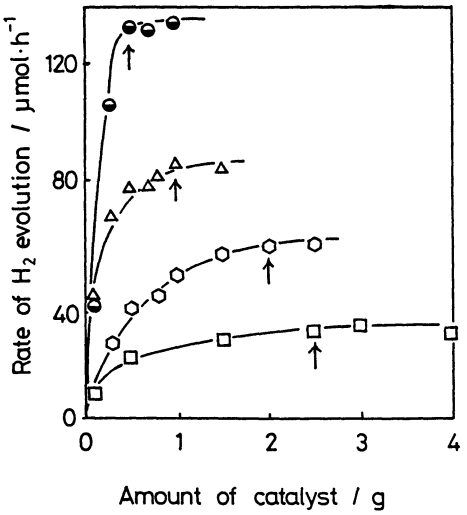

Fig. 5. Dependence of the rates of H_2 evolution from aqueous methanol solution (50 vol%) over various Pt-TiO_2/SiO_2 upon the amounts of catalysts. □: Pt(10 wt%)-TiO_2(0.5 wt%)/SiO_2, ○: Pt(2.5 wt%)-TiO_2(2 wt%)/SiO_2, △: Pt(0.5 wt%)-TiO_2(10 wt%)/SiO_2, ◒: Pt(0.25 wt%)-TiO_2(20 wt%)/SiO_2, solution: 200 ml. Arrows indicate minimum amounts of the catalysts by which the maximum rates of H_2 evolution were shown.

Thus, it is concluded that the activity of the H_2 evolution decreased monotonously with the decrease of the amount of supported TiO_2 over SiO_2. In other words, a higher dispersion catalyst exhibited the quantum efficiency of H_2 evolution lower than the lower dispersion catalyst did. In Table 2, the quantum yields are also summarized. This result is seemingly contra-

Table 2. Comparison of the Maximum Activities over Various TiO_2/SiO_2 Catalysts

Catalysts	Amounts of catalyst[a)	Pt wt%	Amounts of TiO_2 on SiO_2	Rate of H_2 evolution	Quantum yield
	g/200 ml	wt%/TiO_2	g/200 ml	10^{-6} mol · h^{-1}	% at 365 nm
TiO_2(0.5wt%)/SiO_2	2.5	10	0.0125	29	8
TiO_2(2wt%)/SiO_2	2	2.5	0.04	58	16
TiO_2(10wt%)/SiO_2	1	0.5	0.1	86	23
TiO_2(20wt%)/SiO_2	0.5	0.25	0.1	132	35

a) The amounts of catalysts are indicated by arrows in Fig. 5.

dictory to those previously reported, i.e. the high efficiency of highly dispersed TiO_2 in SiO_2[16] and also anchored onto porous Vycor glass[17] for hydrogenation of alkyne with water. The active species for alkyne hydrogenation was regarded as localized electron-hole pairs. On the other hand, in the present case, electrons and holes have to be separated well enough to react with substrates at different sites, i.e. Pt and TiO_2 surfaces. As the detailed structure of the catalyst, Pt-TiO_2/SiO_2, is not clear one can only surmise the explanation of the result. One of the interpretations for the decrease of the activity at low TiO_2 loading region may be the low efficiency of the electron transfer from the conduction band of TiO_2 into Pt particles, which might be caused by the formation of mixed oxide of TiO_2 and SiO_2 due to the calcination at 998 K. If a part of loaded TiO_2 formed the mixed oxide with SiO_2, the diffusion length of the conduction band electron could be reduced and the effect would be more dominant for the lower TiO_2 loading catalyst.

Thus, the high dispersion of a photoactive material over an inert material with a large surface area does not simply result in the increase of the efficiency of the photocatalytic reaction for the "charge-separation" type reaction. To reveal the reason for the low efficiency of the highly dispersed TiO_2 on SiO_2, the detailed structual study of the catalyst will be of importance.

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