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Photoelectrochemical Preparation of Pt/TiO_2 Catalysts

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Pt/TiO_2(anatase) catalysts were prepared by the photoelectrochemical deposition of Pt from hexachloroplatinic acid solution, and their properties for CO and H_2 adsorption were characterized by infrared spectroscopic and volumetric methods. Although the dispersion of Pt deposit depends on the commercial source of TiO_2, the photodeposition of Pt followed by photoreduction with the aid of a sacrificial reducing agent leads to a good result, but the photoelectroplating of Pt in the presence of the reducing agent tends to lower Pt dispersion. The photoimpregnation of hexachloroplatinic acid followed by calcination in air and reduction in H_2 prepares well-dispersed Pt/TiO_2 catalysts irrespective of the source of TiO_2.

INTRODUCTION

Photodeposition of some metals from the solutions of their salts occurs at semiconductor surfaces under irradiation with energy greater than the band gap of semiconductor. Such deposition is based on the photovoltaic effect of semiconducting materials (*1*); band-gap illumination creates hole–electron pairs, and electrons are consumed for the reduction of meal ions while holes for the formation of O_2 from water or the oxidation of counterions. Once a small nucleus of metal is deposited on the semiconductor, it would function as a cathode of a short-circuited photoelectrochemical (PEC) cell (*2*), and the reduction of metal ions takes place around the metal nucleus.

The PEC deposition of metal also occurs on dispersed powders of semiconductors such as TiO_2. Kraeutler and Bard (*3*) applied this to the preparation of supported metal catalysts, Pt supported on TiO_2 and WO_3, and used the Pt/TiO_2 as a photocatalyst for the photoKolbe reaction (*4*). Dunn and Bard (*5*) compared the catalytic activity of the PEC-deposited Pt on TiO_2 for the hydrogenation of benzene with a thermally prepared Pt/TiO_2 catalyst and found that the former shows higher activity than the latter. Mills studied, on the other hand, the photocatalytic activity of variously platinized semiconductor powders for the PEC reaction of EDTA with water (*6*). Although his results depended on the type of semiconductor, the photodeposition method produced photocatalysts of similar activity to those prepared by the method of the precipitation of a platinum sol.

We have recently studied the adsorption of CO on Pt/TiO_2 catalysts prepared by the PEC methods using ir spectroscopy and found that the adsorption amount of CO sensitively depends on the conditions of PEC platinization. We report in this paper an optimum condition of the PEC preparation and a new preparation method of Pt/TiO_2 catalyst which has highly dispersed Pt as compared to those prepared by other methods.

EXPERIMENTAL

TiO_2 was obtained from MCB, Merck, and Kanto Chemicals and used without any pretreatment. The basic procedure of the PEC platinization in our method is as follows: (i) TiO_2 (1.0 g) is suspended in distilled water (100 ml) in a Pyrex beaker (200 ml) and H_2PtCl_6 (51 μmole) is added to the suspension; (ii) a sacrificial reducing agent such as CH_3OH is added in some cases; (iii) the suspension is deaerated by flowing Ar under continuous stirring with a magnetic stirrer and illuminated by a 500-W high-

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pressure Hg lamp (Ushio UIV-570) that is filtered through a bandpass filter (240–400 nm). The completion of the photodeposition (photoadsorption) of H_2PtCl_6 can be detected by a colorimetric method using a uv–visible spectrometer. The resulting slurry is washed with distilled water and dried in a desiccator at room temperature. All the platinized TiO_2 prepared in the present experiment contains 1 wt% Pt.

Since the dispersion of Pt depends on the condition and the procedure of PEC deposition, some variations shown in Table 1 were attempted to examine which factor is important. To avoid misunderstanding, it should be noted that the reducing agents used in the present experiment are not able to reduce H_2PtCl_6 themselves at room temperature. They are so called sacrificial electron donors in PEC and homogeneous photocatalysis systems and function as hole scavengers so as to enhance the photoreduction force of semiconductor. In the absence of sacrificial reducing agent, H_2PtCl_6 disappeared from the illuminated TiO_2 suspension probably due to the photoadsorption or photodecomposition of H_2PtCl_6, but no appreciable Pt deposition was detectable before the addition of reducing agent.

Pt/TiO_2 (MCB, anatase) catalysts were also prepared by standard methods, $NaBH_4$ reduction and impregnation methods, to compare them with the PEC-prepared catalysts. In the former method, H_2PtCl_6 was reduced by a $NaBH_4$ solution (0.1 *M* in 0.1 *N* NaOH solution) under the same condition as in the PEC preparation but in the dark. In the latter method, TiO_2 was immersed in a H_2PtCl_6 solution and, after drying with continuous stirring, calcined in air at 300°C followed by reduction at 350°C in H_2.

For ir measurement, the catalyst was pressed into a self-supporting pellet (40–50 mg, 12 mm diameter). The pellet was outgassed at 230°C in an ir cell with CaF_2 windows, and then ca. 8 Torr (1 Torr = 133.3 N m^{-2}) of CO was introduced into the cell at room temperature. Infrared spectra were recorded with a computing-ratio type ir spectrometer (Hitachi 270-30) with a spectral resolution of ca. 3 cm^{-1}. The background spectra were subtracted using a data processor.

TABLE 1

Conditions of the PEC Preparation of Pt/TiO_2 Catalysts

Method	Procedure
PEC-A	Illumination without any reducing agent for 2 hr and then the addition of HCOOH or CH_3OH (1 ml)
PEC-B	Illumination in the presence of HCOOH (1%) for 30 min
PEC-C	Illumination in the presence of CH_3OH (1%) for 30 min
PEC-D	Illumination in the presence of CH_3COOH (1%) for 2 hr

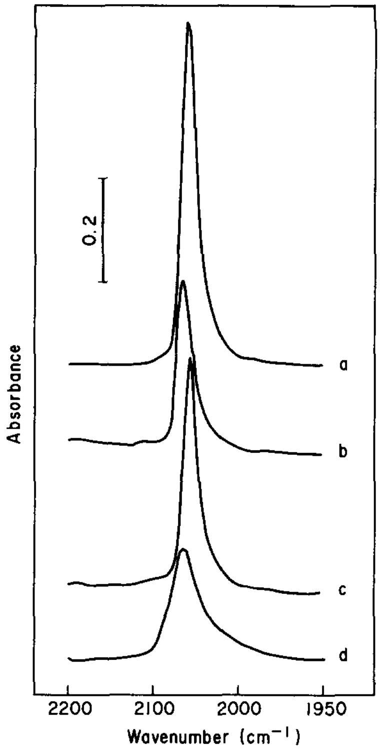

FIG. 1. Infrared spectra of CO adsorbed on Pt/TiO_2(MCB) catalysts prepared by various methods. (a) PEC-A; (b) PEC-B; (c) $NaBH_4$ reduction; (d) impregnation and H_2 reduction.

The adsorption amounts of H_2 and CO were measured in an apparatus of the BET measurement. The samples (0.5 g) were reduced by H_2 at 200°C prior to the adsorption measurement.

RESULTS

PEC Preparation Methods

Figure 1 shows the observed ir spectra of CO adsorbed on Pt/TiO_2 (MCB, anatase) prepared by various methods. Spectra a and b correspond to PEC-A and PEC-B, respectively, and spectra c and d correspond to the reference preparation methods, the $NaBH_4$ reduction and the impregnation methods, respectively. Clearly, the spectral intensity of adsorbed CO on the catalysts depends on the conditions of PEC preparation. The spectral intensity for each sample was reproducible within the experimental error of about ±10% as far as the amount of sample is the same. The integrated absorbance measurements are summarized in Table 2. It is convenient to assume that the amount of adsorbed CO is indicated by the ir absorbance, though the quantitative relation between them is not exactly linear (*7*, *8*). The results of Table 2 show that the amount of adsorbed CO, i.e., the dispersion of Pt decreases in the sequence, PEC-A > $NaBH_4$ reduction > H_2 reduction > PEC-B. PEC-C gives a result identical to PEC-B while PEC-D is the same as PEC-A. Hydrogen reduction of the PEC prepared catalysts at 300°C had no effect on the amount of CO adsorption, indicating that PEC-deposited Pt is completely reduced.

TABLE 2

Integrated ir Absorbance (cm^{-1}) of Adsorbed CO

Spectrum	Fig. 1	Fig. 2	Fig. 4
a	18	8	38
b	9	13	40
c	13	11	
d	11	15	

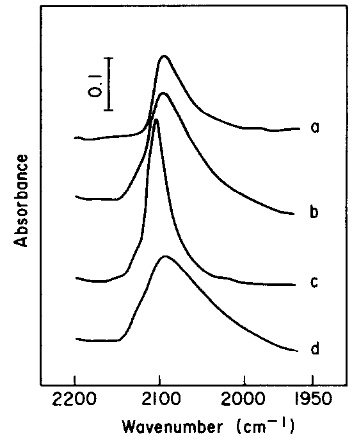

FIG. 2. Infrared spectra of CO adsorbed on Pt/TiO_2 (Merck) catalysts prepared by various methods. (a) PEC-A; (b) same as PEC-A but with O_2 bubbling prior to the addition of CH_3OH; (c) same as PEC-A but with intermittent bubbling of O_2 after the addition of CH_3OH; (d) $NaBH_4$ reduction.

One may note that the ir absorption band of CO adsorbed on the PEC-prepared Pt/TiO_2 is fairly sharp; the half-width of the band is less than 25 cm^{-1} whereas it is ca. 40 cm^{-1} on the catalysts prepared by the impregnation method. This fact suggests that the property of Pt deposit on the PEC-prepared catalysts is homogeneous, since adsorbed CO on Pt single crystals gives a sharp ir absorption band with the half-width of ca. 10 cm^{-1} (*7*).

The method of PEC-A is also successful for Kanto TiO_2(anatase) but not for Merck TiO_2(anatase). Figure 2 shows the ir spectra of CO adsorbed on Pt/TiO_2(Merck) catalysts and the integrated absorbances are given in Table 2. In this case PEC-A and PEC-D bring about almost the same result as PEC-B and PEC-C, i.e., no merit in PEC-A and PEC-D. In an attempt to improve these methods, it was found that PEC-A is somewhat improved when O_2 is bubbled into the suspension before the addition of CH_3OH (spectrum b in Fig. 2), but the amount of CO adsorption does not exceed that on the catalyst prepared by the $NaBH_4$ reduction (spectrum d). The intermittent bubbling of O_2 after the addition of

CH_3OH improves the sharpness of the ir band of adsorbed CO (spectrum c) but results in a small shift of the band to higher frequency, indicating the weak oxidation of Pt (*15, 16*).

The difference between MCB and Merck TiO_2 in the PEC deposition of Pt was investigated. Figure 3 shows the time dependence of the photodecomposition (photoadsorption) of H_2PtCl_6 on MCB and Merck TiO_2. In this experiment, a small amount of TiO_2 was suspended in a dilute solution of H_2PtCl_6. The solution was sampled at appropriate intervals during illumination. The sample was centrifuged to remove TiO_2, and the concentration of H_2PtCl_6 was determined by a colorimetric method. The result shows that there is no difference in the decreasing rate of H_2PtCl_6 concentration, i.e., no difference in the photocatalytic activity. One difference is in the suspension of particles in the solution after illumination. For MCB and Kanto TiO_2, the suspended particles precipitate after illumination in H_2PtCl_6 solution while Merck TiO_2 is still suspended well even after prolonged illumination and begins to precipitate after the addition of the reducing agent.

The photodecomposition (photoadsorption) of H_2PtCl_6 also occurs on rutile without a reducing agent, but after the completion of the photoadsorption the photodeposition of Pt metal is not detected even after the addition of HCOOH, probably because rutile has more positive flat band potential than anatase so that the reduction force of rutile is smaller than that of anatase (*4*). The methods of PEC-B and PEC-C are, however, useful for the Pt photodeposition on rutile.

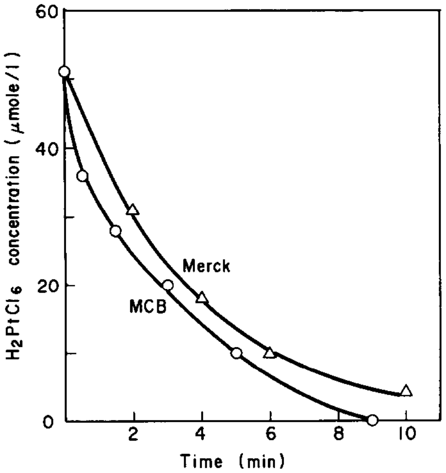

FIG. 3. Time course of the photodecomposition of H_2PtCl_6 on TiO_2. 10 mg TiO_2 + 2.6 μmole H_2PtCl_6 in 50 ml H_2O.

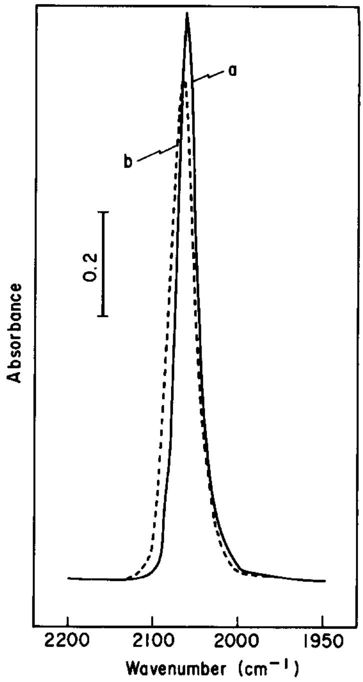

FIG. 4. Infrared spectra of CO adsorbed on Pt/TiO_2 catalysts prepared by the photoimpregnation method. (a) $MCBTiO_2$; (b) Merck TiO_2.

Photoimpregnation Method

To examine the dispersion of the adsorbed Pt chlorides on TiO_2, the suspension of TiO_2 was filtered after the photodecomposition of H_2PtCl_6 without sacrificial reducing agent, and the TiO_2 was calcined in air at 300°C and reduced by H_2 at 350°C in the ir cell. The Pt dispersion of this sample is fairly high; the integrated ir absorbance of adsorbed CO is twice as large as that observed on the $Pt/TiO_2(MCB)$ prepared by PEC-A (Fig. 4 and Table 2). Furthermore, this method is also successful for Merck

TiO_2 as shown in Fig. 4. Thus the combination of photo and thermal processes is appeared to be an excellent method for the preparation of Pt/TiO_2 catalysts. We will refer to this method as the photoimpregnation method. The results of Fig. 4 and Table 2 indicate that the adsorbed Pt chlorides are well dispersed on TiO_2 and that the photoreduction in the presence of the reducing agent lowers Pt dispersion.

Adsorption Amounts of H_2 and CO

The adsorption amounts of H_2 and CO on Pt/TiO_2 catalysts were volumetrically measured. The results are summarized in Table 3. In accordance with the ir measurement, the adsorption amount of H_2 on the PEC-prepared catalysts is larger for PEC-A than for PEC-B, but PEC-A did not yield better result than the standard impregnation method. The photoimpregnation method is excellent for both H_2 and CO adsorption as expected from the ir measurements. Since H/Pt ratio exceeds unity in this case, H_2 adsorption may involve the spillover of adsorbed hydrogen from Pt to TiO_2.

DISCUSSION

The difference in Pt dispersion in the PEC deposition methods may be interpreted in terms of the following mechanisms. When a sacrificial reducing agent is present, photogenerated holes on TiO_2 react with the reducing agent so that TiO_2 particles are negatively charged (potential floating effect) (*9*, *10*). As a result, photogenerated electrons easily reduce H_2PtCl_6 to Pt metal, which deposits on TiO_2 surface. The Pt deposit then functions as a cathode, on which H_2 is evolved by the PEC mechanism (*11*, *12*), and therefore, Pt tends to plate out around the original Pt deposit, leading to ill-dispersed Pt. In addition to this PEC mechanism, there would be a homogeneous reaction mechanism. When the reducing agent such as alcohol is partially oxidized by holes, reactive intermediates (radicals) which are able to reduce H_2PtCl_6 to Pt are produced in the solution. Pt metal thus formed in the solution would tend to agglomerate before adsorption on TiO_2. Therefore, this mechanism also results in ill-dispersed Pt.

TABLE 3

Adsorption Amounts of H_2 and CO on Pt/TiO_2(MCB) Catalysts

Preparation method	H_2[a] (ml STP/g)	H/Pt[b]	CO (ml STP/g)
PEC-A	0.28	0.5	—
PEC-B	0.1	0.2	—
Impregnation			
Standard	0.30	0.5	0.18
Photo	1.4	2.5	0.50

[a] Adsorption amount at ca. 50 Torr.

[b] Number of H atoms per one Pt atom.

Although one may suspect that CH_3COOH behaves as a sacrificial reducing agent like HCOOH or CH_3OH, the former has more positive electrochemical oxidation potential than the latter and, therefore, is not easily oxidized. In addition, CH_3COOH is photodecomposed to mainly CH_4 and CO_2 on TiO_2 or Pt/TiO_2 (photo-Kolbe reaction) (*4*, *14*) and CH_4 is hardly oxidized. In fact, it takes much longer time in PEC-D to reduce Pt completely than in PEC-B and PEC-C. The mehanism involved in PEC-D is probably similar to that involved in PEC-A. This is probably the reason that Bard *et al.* obtained highly active Pt/TiO_2 catalysts by their PEC method, in which the photodeposition was carried out in a CH_3COOH/CH_3COONa buffer solution (*3*, *5*).

In the absence of the reducing agent, on the other hand, H_2PtCl_6 seems to be photodecomposed to Pt chlorides (ions) which adsorb on TiO_2, viz.,

$$H_2PtCl_6 \xrightarrow[TiO_2]{h\nu} PtCl_4 + 2HCl \qquad (1)$$

$$PtCl_4 \rightarrow PtCl_4(a) \qquad (2)$$

The formation of HCl was assumed from the decrease in pH of the solution from 3.0 to 2.5 in PEC-A but the formation of $PtCl_4$

was not confirmed. The adsorbed Pt chlorides would be well dispersed since the adsorption may occur on the bare site of TiO_2 surface. The addition of the reducing agent after this process brings about the reduction of the adsorbed Pt chlorides, resulting in fairly dispersed Pt. In fact, this was clearly demonstrated by the photoimpregnation method. PEC-A is, however, still much inferior in Pt dispersion to the photoimpregnation method, indicating that the photoreduction of the Pt chlorides gives rise to the agglomeration of Pt metal on the TiO_2 surface. The adsorbed Pt chlorides may be somewhat mobile on the TiO_2 surface so that they tend to be reduced around Pt metal by the PEC mechanism. In the photoimpregnation method, the Pt chlorides are fixed to the TiO_2 surface by drying and calcination, and as a result the dispersion remains unchanged after the reduction.

Merck TiO_2(anatase) was unsuitable for PEC-A probably due to its surface properties. The photoimpregnation method revealed that the Pt chlorides on Merck TiO_2 are well dispersed after the illumination with no sacrificial reducing agent. Therefore, the agglomeration of Pt metal takes place after the addition of the reducing agent. The adsorbed Pt chlorides may be more mobile on Merck TiO_2 than on other TiO_2. The bubbling of O_2 before the addition of reducing agent in PEC-A would lead to the photooxidation of the Pt chlorides and somewhat serve to fix them to the TiO_2 surface and to improve Pt dispersion (see spectrum b in Fig. 2). The photooxidized Pt chlorides may be photoreduced after the addition of the sacrificial agent.

In summary, the PEC preparation of Pt/TiO_2 catalysts is not necessarily superior to other thermal preparation methods with respect to CO and H_2 adsorption properties. The dispersion of Pt on the catalysts strongly depends on the preparation methods and the source (manufacturer and crystal structure) of TiO_2. The photoreduction of Pt is, however, attractive in a sense to avoid strong metal–support interaction (*17*) which appears in high-temperature reduction, and the property of photodeposited Pt is expected to be homogeneous from the ir measurements.

On the other hand, the photoimpregnation method, a new method proposed in this paper, is probably one of the best methods to prepare highly dispersed Pt/TiO_2 catalysts irrespective of the source of TiO_2, especially when the standard methods do not produce high dispersion. The properties of the Pt/TiO_2 for CO and H_2 adsorption are excellent and the surface homogeneity of Pt is suggested from the sharp ir absorption band of adsorbed CO. This method may be applied to the preparation of other metal/semiconductor catalysts.

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