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XPS Studies of the Platinum Species Photodeposited on Titania from Aqueous Chloroplatinic Acid

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Synopsis. Several Pt/TiO_2 catalysts were prepared by photodeposition from aqueous H_2PtCl_6 in the presence or absence of a CH_3COOH-CH_3COONa buffer. The examination of these catalysts by X-ray photoelectron spectroscopy (XPS) revealed that the higher the buffer concentration, the more highly reduced the deposited platinum became.

Platinum-loaded titania (Pt/TiO_2) is known as the most active catalyst in a number of photocatalytic processes. As a means of platinum loading, the photodeposition method of Kraeutler and Bard[1)] has been widely used. In this method, the platinizing solution contains acetate, which is considered to act as the reducing agent. Although these authors claimed that the platinum deposit is really metallic, Koudelka *et al.*[2)] found no perceptible quantities of metallic platinum on their Pt/TiO_2 samples, which had been prepared by a similar method. Lehn *et al.*,[3)] on the other hand, photodeposited platinum from aqueous K_2PtCl_4 on $SrTiO_3$ without adding any organic material.

It thus seemed expedient to prepare a series of Pt/TiO_2 catalysts from aqueous H_2PtCl_6 solutions containing different concentrations of a CH_3COOH-CH_3COONa (AH–ANa) buffer and to examine the oxidation state of the platinum deposit. It would also be interesting to see how the platinum oxidation state of these catalysts varies after their use in typical photosynthetic or photocatalytic reactions. Methanol decomposition and benzene oxidation have been chosen for this purpose.

Experimental

Apparatus. The platinum oxidation state of Pt/TiO_2 catalysts was examined by means of a Hewlett-Packard 5950A X-ray photoelectron spectrometer with monochromatized Al *Kα* X-rays (1486.6 eV). Spectra were recorded at 250 K with a flood gun. The binding energies E_b are referred to the $4f_{7/2}$ peak (84.0 eV) of the Au evaporated onto the sample.

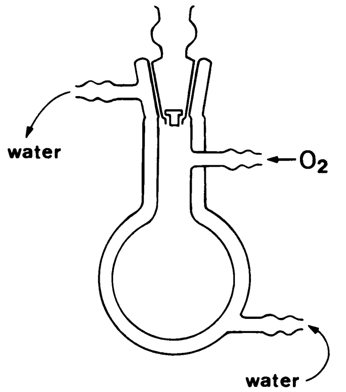

Fig. 1. Reaction vessel II (Water-mantled Pyrex-made).

The lamp-housing quartz reaction vessel (I) used for the platinum photodeposition and methanol decomposition has been described previously.[4)] The water-mantled Pyrex reaction vessel (II) used for benzene oxidation is illustrated in Fig. 1. It has a capacity of *ca.* 50 cm³. The reaction products of the benzene oxidation were analyzed by means of gas chromatography using a 2 m×3 mm i.d. column of 30% PEG 20M on 30—60 mesh chromosorb WAW.

Materials. The rutile-free anatase, with a BET surface area of 11.5 m²/g, was taken from the same bottle as had been used previously.[4)] All the chemicals except for Adams platinum were commercially available and were used as received. The Adams platinum, whose main constituent had been verified to be α-PtO_2 by X-ray powder diffraction, was generously supplied by Professor Takagi of Nihon University.

Catalyst Preparation. The procedure for preparing Pt/TiO_2 catalysts (2.5 wt% Pt) has been presented before.[4)] In brief, they were prepared by the photodeposition of platinum on TiO_2 from aqueous TiO_2 suspensions containing H_2PtCl_6 and an AH–ANa buffer (pH 4.07). The buffer concentration was varied from catalyst to catalyst, while the H_2PtCl_6 concentration was fixed so as to give 2.5 wt% of Pt for all catalysts.

Kinetic Procedure. The methanol decomposition was run in reaction vessel I. It was charged with the Pt/TiO_2 catalyst (50 mg), methanol (100 cm³), and distilled water (100 cm³). After 30-min N_2 bubbling with magnetic stirring, this reaction mixture was irradiated with a 100-W high-pressure Hg lamp for 1 h at 40 °C, with continued magnetic stirring.

The benzene oxidation was run in reaction vessel II. It was charged with water (10 cm³), benzene (1 cm³), and the Pt/TiO_2 catalyst (50 mg), set on a shaker, and connected to an atmospheric O_2 bulb. The reaction mixture was irradiated at 20 °C for 3 h with vigorous shaking with a 500-W Xe lamp, using two filters, UV-33 and IRA-25S, in series. After the reaction, acetic acid (15 cm³) was added to make the reaction mixture homogeneous, and aliquots were analyzed for phenol.

Results

Oxidation State of the Photodeposited Pt. All of the catalyst samples prepared were examined by means of XPS. The XPS spectra are shown in Fig. 2A. The molar ratios $(AH+ANa)/H_2PtCl_6$ pertaining to each catalyst preparation are given in Table 1. A comparison of the XPS spectra with these molar ratios reveals that the lower the ratio, the more oxidized state the deposited platinum remains in.

Figure 2B shows the Pt 4f spectra taken with a Pt plate and PtO_2 powders, together with the standard E_b values ($4f_{5/2}$ and $4f_{7/2}$) for Pt^0 and Pt^{IV} determined from these spectra. The corresponding values for Pt^{II} obtained with PtO are 76.6 and 73.4 eV, according to Kim *et al.*[5)] Turning back to Fig. 2A, we see that the triplet character (peaks at 73.5, 76.0, and 78.8 eV) of Sample 5 prepared from a buffer-free suspension is

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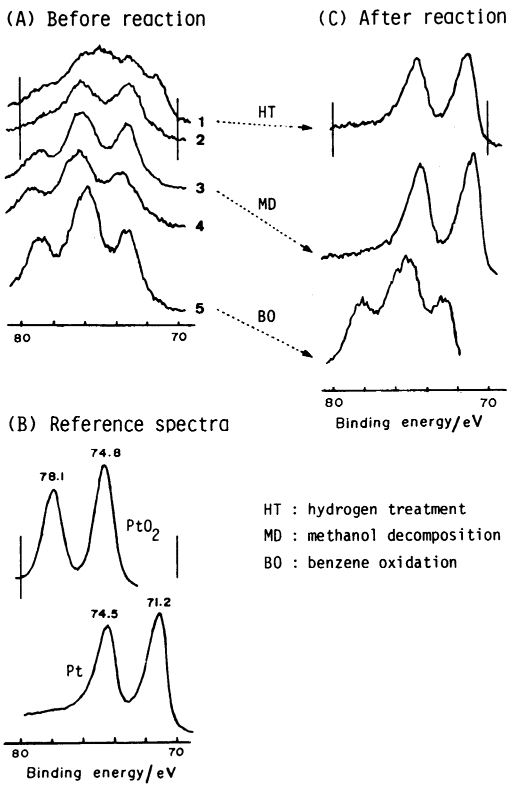

Fig. 2. XPS spectra in the Pt 4f region of Pt/TiO_2 catalysts.

Table 1. The effects of the acetate buffer-to-Pt complex ratio in Pt/TiO_2-catalyst preparation

Sample	$\frac{AH+ANa^{a)}}{H_2PtCl_6}$	MOS[b)]	$\frac{X^{c)}}{\%}$
1	30.4	0+II	
1-HT[d)]		0	0.69
2	10.1	II	0.17
3	6.1	II+IV	
4	2.0	II+IV	
5	0	II+IV	0.10

a) The molar ratio of acetic acid (AH) plus sodium acetate (ANa) to hexachloroplatinic acid (H_2PtCl_6). AH/ANa=4.56, giving rise to a pH of 4.07. b) The main oxidation states of the deposited platinum, judged from the XPS spectra of Fig. 2. c) Percentage conversion of benzene to phenol. d) Hydrogen-treated sample 1 (*cf.* Fig. 2).

attributable to the partial overlap of the two doublets of the Pt^{II} and Pt^{IV} species; the Pt^{II} $4f_{5/2}$ and Pt^{IV} $4f_{7/2}$ components are superimposed on each other. Upon the addition of an acetate buffer (Sample 3 or 4), the left-wing peak of the triplet became smaller, while the right one was intensified, suggesting the enrichment of the Pt^{II} components. Upon going to a higher buffer concentration (Sample 2), only the Pt^{II} species became predominant. A still further increase in the buffer concentration (Sample 1) resulted in an ill-defined spectrum, which, however, suggests the appearance of Pt^0. The main platinum oxidation states thus estimated from Fig. 2A for each catalyst are listed in Table 1.

The Cl/Pt molar ratio of the photodeposited species was less than 0.7, judging from the area under the Cl 2s peak. This is a much smaller amount of chlorides than would be expected from the $PtCl_6^{2-}$ or $PtCl_4^{2-}$ adsorption; it is in qualitative agreement with the results of Koudelka *et al.*[2)], who found a Cl/Pt ratio<1.

Photodeposition Process. From the above results, it may be concluded that the photodeposition from aqueous H_2PtCl_6 on TiO_2 does not yield Pt^0 unless acetate is present in a large excess relative to the platinum complex. Even in a large excess of it, the deposited platinum species tend to remain partially in oxidative states, Pt^{II} and Pt^{IV}. In view of the above-mentioned dearth of chloride, these oxidative species must exist as oxides, hydroxides, or chloride oxides rather than as the tetra- or hexachloroplatinate.

On the basis of these findings, one may speculate that these steps occur in photodeposition: (i) the adsorption of $PtCl_6^{2-}$ and $PtCl_4^{2-}$ ions, (ii) the rapid conversion of these chlorides to the oxides or hydroxides, and (iii) their photo-assisted reduction to Pt^0. The mechanism of each step is not yet clear, however.

Pt Oxidation State after Reactions. Figure 2C shows how the Pt 4f spectra of the Pt/TiO_2 catalysts vary after their use or after hydrogen treatment. A comparison of Fig. 2A with Fig. 2C (Samples 1 and 3) reveals that the oxidized platinum is easily reduced to Pt^0 by either mild hydrogen treatment (1 atm, 1.5 h, 20 °C in water) or subjection to methanol decomposition. The reduction due to methanol decomposition seems reasonable in view of the expected occurrence of hydrogen recombination on the platinum surface:

$$2H^+ + 2e^- \rightarrow H_2. \qquad (1)$$

In contrast, the subjection of Catalyst 5 to benzene oxidation did not cause any appreciable change in the XPS spectrum. This intactness might result from a subtle balance between the reductive trend due to the H_2 produced by Reaction 1 and the oxidative trend due to the O_2 or H_2O_2 involved in this reaction:

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2. \qquad (2)$$

The last column of Table 1 compares the catalytic activities of three different catalyst samples for benzene oxidation. The H_2-treated sample (1-HT) bearing only Pt^0 is prominent, exhibiting an activity which is several times that of the other two. This rather unexpected effect of Pt^0 remains to be elucidated.

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