ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 87 (1995) 249–255

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

Effects of H^+, Cl^- and CH_3COOH on the photocatalytic conversion of $PtCl_6^{2-}$ in aqueous TiO_2 dispersion

Chanjuan Xi, Zhengshi Chen, Qinglin Li, Zhensheng Jin *

Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

Received 20 September 1994; accepted 18 October 1994

Abstract

In this work, the effects of H^+, Cl^- and CH_3COOH on the photocatalytic conversion of $PtCl_6^{2-}$ in an aqueous TiO_2 dispersion were studied by means of X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), UV–visible diffuse reflectance spectroscopy and UV–visible absorption spectroscopy. The results obtained show that $PtCl_6^{2-}$, in the form of its hydrolysis product, is photocatalytically converted into a solid deposit on the TiO_2 surface; the quantity and composition of the solid deposit vary with the degree of $PtCl_6^{2-}$ hydrolysis. When both H^+ and Cl^- concentrations are sufficiently high to depress the hydrolysis of $PtCl_6^{2-}$, no deposit is observed on the TiO_2 surface. The effect of CH_3COOH on the composition of the photocatalytic product of $PtCl_6^{2-}$ on the TiO_2 surface is closely related to the degree of ionization of CH_3COOH.

Keywords: Photocatalytic conversion; TiO_2 dispersion; $PtCl_6^{-2}$ hydrolysis

1. Introduction

Bard and coworkers [1,2] were the first to report the preparation of a Pt^0/TiO_2 catalyst by photocatalytic reduction of $PtCl_6^{2-}$ in the presence of CH_3COOH. They suggested that CH_3COOH (a hole scavenger) was beneficial to the reduction of $PtCl_6^{2-}$ to Pt^0

$$CH_3COO^- + h^+ \longrightarrow CO_2 + {}^{\bullet}CH_3 \quad (1)$$

$$PtCl_6^{2-} + 4e^- \longrightarrow Pt^0 + 6Cl^- \quad (2)$$

This method for the preparation of Pt^0/TiO_2 catalyst was widely adopted [3–6]. Curran et al. [7] studied the kinetics of the photocatalytic conversion of $PtCl_6^{2-}$ on TiO_2. CH_3COOH was not added to the dispersion, and the residual $PtCl_6^{2-}$ after illumination was analysed by atomic absorption spectroscopy. They reported the product to be Pt^0 under various conditions. However, the deposit on the TiO_2 surface was not identified. Koudelka et al. [8] used similar conditions to those in Ref. [1] to process the photoreaction of $PtCl_6^{2-}$ on the TiO_2 surface film of a Ti rod and obtained a deposit containing Pt^{4+} and Pt^{2+} compounds. It was suggested that they were produced by hydrolysis of $PtCl_6^{2-}$, and were converted to Pt^0 on cyclovoltammetric scanning.

A very important point was ignored in all of the abovementioned studies, namely the relationship between the hydrolysis of $PtCl_6^{2-}$ and the photocatalytic reaction. As early as the 1960s and 1970s, Blasius et al. [9] and Cox et al. [10] observed the hydrolysis of $PtCl_6^{2-}$ in aqueous solution

$$\left.\begin{array}{l} PtCl_6^{2-} + H_2O \rightleftharpoons Pt(OH)Cl_5^{2-} + H^+ + Cl^- \\ Pt(OH)Cl_5^{2-} + H_2O \rightleftharpoons Pt(OH)_2Cl_4^{2-} + H^+ + Cl^- \\ \vdots \\ Pt(OH)_3Cl_3^{2-} + H_2O \rightleftharpoons Pt(OH)_4Cl_2^{2-} + H^+ + Cl^- \end{array}\right\} \quad (3)$$

Hydrolysis can take place in HCl (3–0.1 N). In 0.05 N HCl, 20% of $PtCl_6^{2-}$ is converted to $Pt(OH)Cl_5^{2-}$, and in 0.01 N HCl to neutral solution, $Pt(OH)_2Cl_4^{2-}$ is formed in addition to $Pt(OH)Cl_5^{2-}$. In neutral and basic solution (up to 0.1 N NaOH), the final hydrolysis product contains both $Pt(OH)_5Cl^{2-}$ and $Pt(OH)_6^{2-}$. The hydrolysis equilibrium is accelerated by UV illumination. Our study on the absorption spectrum of aqueous $PtCl_6^{2-}$ solution at different pH values also confirms the abovementioned experimental results [11].

---

* Corresponding author.

SSDI 1010-6030(94)03983-6

In this paper, the effects of H^+, Cl^- and CH_3COOH on the photocatalytic conversion of $PtCl_6^{2-}$ in a TiO_2 dispersion are reported. The results obtained indicate that the explanations given in the literature for the photocatalytic reaction mechanism are not appropriate.

2. Experimental details

2.1. Reagents

TiO_2 powder (anatase, 99%) was the product of Fluka AG (packed in Switzerland). $H_2PtCl_6 \cdot H_2O$, NaCl and CH_3COOH were analytical grade reagents (China).

2.2. Photodeposition

2 g TiO_2, 1.32 ml of H_2PtCl_6 (0.077 M) and an appropriate amount of distilled water (or 0.1 M CH_3COOH) were added to a 60 ml round-bottomed flask to give a total dispersion volume of 20 ml. The pH of the dispersion ($pH \approx 2.4$) can be adjusted with NaOH solution to the desired value. Air dissolved in the dispersion was expelled by purging with pure N_2. After 15 min, the system was closed and illuminated. During illumination, gas samples were taken for analysis after fixed times. A 250 W high pressure Hg lamp was used as light source (see Fig. 1). After illumination, the solid sample was rinsed by decanting until no Cl^- was detected in the supernatant liquid. The sample was dried in a vacuum oven at about 100 °C for 2 h and then stored in a desiccator.

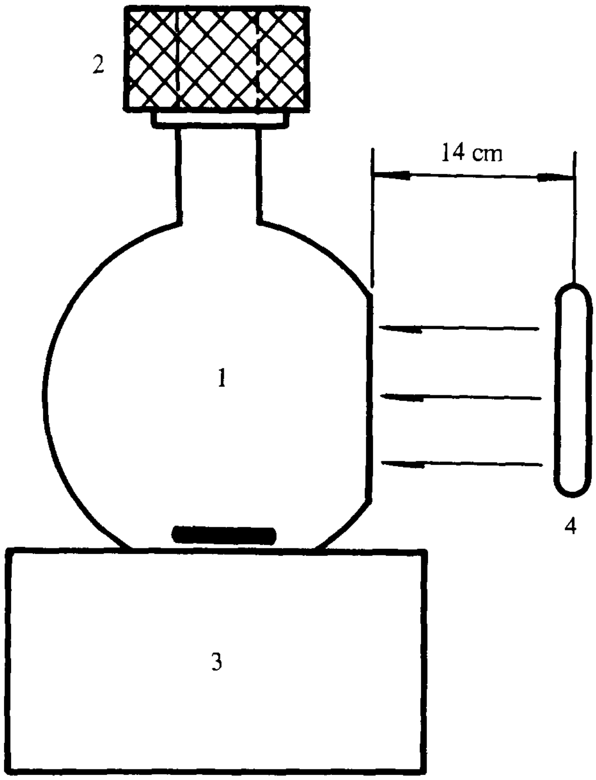

Fig. 1. Device for photoillumination: 1, reaction bottle; 2, sealing; 3, magnetic stirrer; 4, high pressure Hg lamp (250 W).

2.3. Analysis of deposit

X-Ray photoelectron spectroscopy (XPS) of the deposit was performed using a PHI-550 multitechnique spectrometer (P-E Co.). The composition of the deposit and the valencies of Pt were ascertained according to Ref. [11]. The relative atomic concentration on the TiO_2 surface was calculated using a computer program supplied by P-E Co. The error in the binding energy measurements was approximately 0.3 eV. Ti $2p_{3/2}$ ($E_b = 459$ eV) and C 1s contamination were taken as reference standards.

A P-E DSC-2C (USA) instrument was used for differential scanning calorimetry (DSC) and a P-E TGS-2 (USA) instrument for thermogravimetric analysis (TGA). UV–visible diffuse reflectance spectra were recorded on a Shimadzu UV-365 (Japan).

2.4. Analysis of solution

A PHS-10A digital acidimeter (China) was used for pH measurements, with an accuracy of ±0.02 pH units. UV–visible absorption spectra were taken with a Shimadzu UV-240 (Japan).

3. Results and discussion

3.1. Effect of pH

With an initial concentration of H_2PtCl_6 of 5.1×10^{-3} M, corresponding to $Pt:TiO_2 = 1:100$ w/w, different deposits on the TiO_2 surface were obtained by changing the pH of the dispersion (Table 1, Fig. 2). The deconvolution results of Fig. 2(a) indicate that the deposit from test 1 is composed of two Pt compounds. With reference to the binding energies of Pt $4f_{7/2}$ given in the literature (Table 2), Pt $4f_{7/2} = 75.0$ eV can be attributed to PtO_2 and Pt $4f_{7/2} = 72.9$ eV to $Pt(OH)_2$. Pt $4f_{7/2} = 72.8$ eV in both Figs. 2(b) and 2(c) can be attributed to $Pt(OH)_2$. The different photodeposits on the TiO_2 surface as a function of the pH value are also displayed by DSC and UV–visible diffuse reflectance spectroscopy. The DSC measurement was carried out in an atmosphere of high purity N_2. Raw TiO_2 began to absorb heat above 500 °C (Fig. 3(a)) (desorption of chemically bound water on the TiO_2 surface), whereas the test 1 sample gave an exothermic peak at 226 °C and then slowly absorbed heat above 300 °C (Fig. 3(b)). The test 2 sample gave no exothermic peak (Fig. 3(c)), but showed the same heat absorption as that in Fig.

Table 1
Effect of pH on the photoconversion of the $PtCl_6^{2-}$ in aqueous TiO_2 dispersion

Test	pH (before illumination)	Initial $[H_2PtCl_6]$ (M)	Time of illumination (h)	Photodeposit	Relative surface Pt concentration (%)	Remarks
1	11.92	5.1×10^{-3}	5	$PtO_2+Pt(OH)_2$ (36:64)	1.4	
2	6.67	5.1×10^{-3}	5	$Pt(OH)_2$	1.1	
3	2.40	5.1×10^{-3}	5	$Pt(OH)_2$	0.4	Trace H_2 formed at initial stage

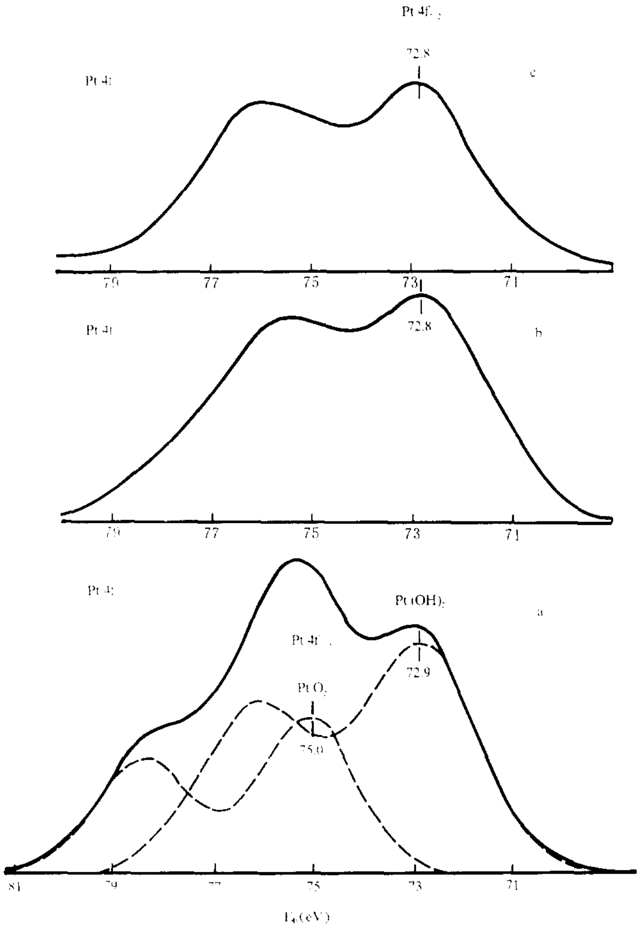

Fig. 2. Effect of pH on photodeposit: (a) pH 11.92; (b) pH 6.67; (c) pH 2.40.

Table 2
Binding energies of Pt $4f_{7/2}$ in several platinum compounds

Pt	$Pt(OH)_2$	PtO	PtO_2	K_2PtCl_6	Reference
71.0	72.4	72.2	74.4		[12]
71.2		72.5	74.6		[13]
70.9		72.2			[14]
70.7			74.2		[15]
71.1				75.7	[8]
71.2	72.6		74.8	75.5	[11]

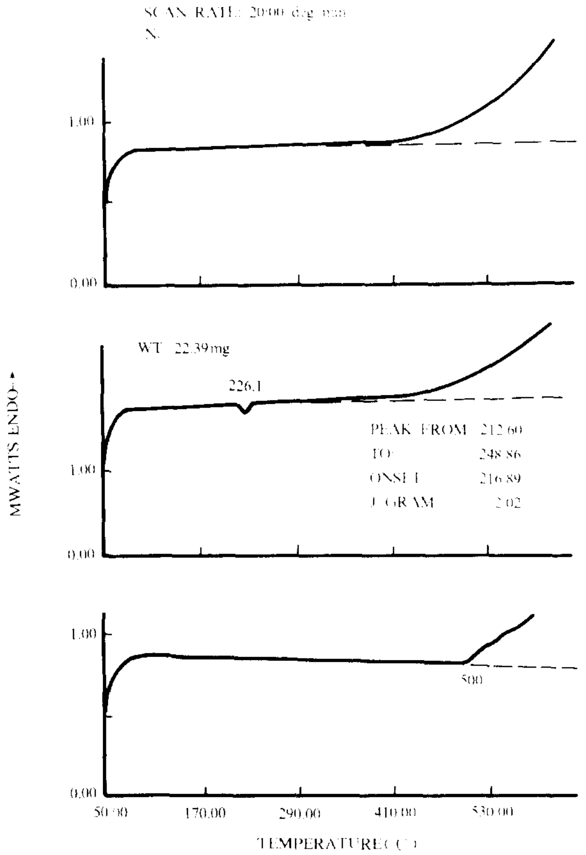

Fig. 3. DSC: (a) raw TiO_2; (b) $(PtO_2+Pt(OH)_2)/TiO_2$; (c) $Pt(OH)_2/TiO_2$.

3(b). PtO_2 is unstable and begins to decompose around 200 °C [11]

$$PtO_2 \longrightarrow Pt+O_2 \qquad (4)$$

From the thermogram in Fig. 4, a weight-losing peak corresponding to the exothermic peak of Fig. 3(b) is observed and confirms the decomposition of PtO_2. No report is available on the decomposition heat of PtO_2. Assuming that the platinum loaded on TiO_2 amounts to 1% of the total weight and 36 at.% takes the form of PtO_2, the decomposition heat can be estimated as 18 kcal mol^{-1}. Platinous hydroxide decomposes above 300 °C, leading to an endothermic reaction [16]

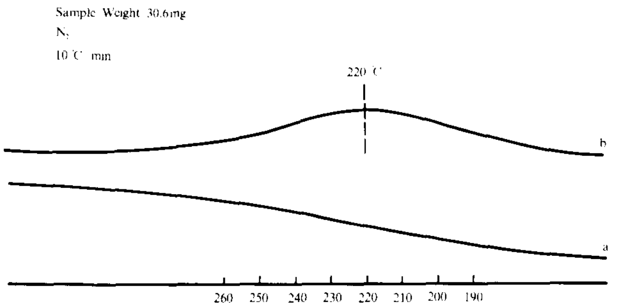

Fig. 4. Thermogram of $(PtO_2+Pt(OH)_2)/TiO_2$: (a) integral; (b) differential.

$$Pt(OH)_2 \xrightarrow{\Delta} PtO + H_2O \xrightarrow{>550\ ^\circ C} Pt^0 + \tfrac{1}{2}O_2 \qquad (5)$$

Fig. 5 shows the UV–visible diffuse reflectance spectra of deposited Pt on the TiO_2 surface. Fig. 5(b) shows a shoulder at $\lambda = 425$ nm. This shoulder disappears when the deposit is heated at 230 °C for 30 min in a pure N_2 atmosphere (Fig. 5(b′)). In XPS (Fig. 6(b)), the 75.0 eV peak is replaced by a peak of Pt^0 (Pt $4f_{7/2} = 71.0$ eV). This indicates that the shoulder in Fig. 5(b) is characteristic of PtO_2. After heating the sample at 620 °C for 30 min, the surface deposit is converted to Pt^0 completely (Fig. 6(c)).

In an investigation of the relationship between O_2 liberation from an aqueous Pt^0/CdS dispersion and the amount of $PtCl_6{}^{2-}$ added, we discussed the mechanism of PtO_2 and $Pt(OH)_2$ formation. When TiO_2 was used instead of Pt^0/CdS, the same deposit was obtained under similar experimental conditions (except the light source) [11]. This indicates that a similar mechanism of $PtCl_6{}^{2-}$ photocatalytic conversion exists for both semiconductor powders.

(1) In basic medium (test 1), the concentration of the hydrolysis product $Pt(OH)_4Cl_2{}^{2-}$ in Eq. (3) is high and it can accept four photogenerated h^+ on TiO_2 to form PtO_2

$$Pt(OH)_4Cl_2{}^{2-} + 4h^+ \longrightarrow PtO_2 + O_2 + 4H^+ + 2Cl^- \qquad (6)$$

while $Pt(OH)_2Cl_4{}^{2-}$ (and/or $Pt(OH)Cl_5{}^{2-}$) accepts two photogenerated e^- to form $Pt(OH)_2$

$$Pt(OH)_2Cl_4{}^{2-}(Pt(OH)Cl_5{}^{2-} + OH^-) + 2e^- \longrightarrow Pt(OH)_2 + 4Cl^-(5Cl^-) \qquad (7)$$

(2) In less basic or acidic medium, $Pt(OH)_2Cl_2{}^{2-}$ (and/or $Pt(OH)Cl_5{}^{2-}$) is the main hydrolysis product of $PtCl_6{}^{2-}$ and gives only the reduction product $Pt(OH)_2$ on the TiO_2 surface after illumination. Cameron and Bocarsly [17] studied the homogeneous photoinduced

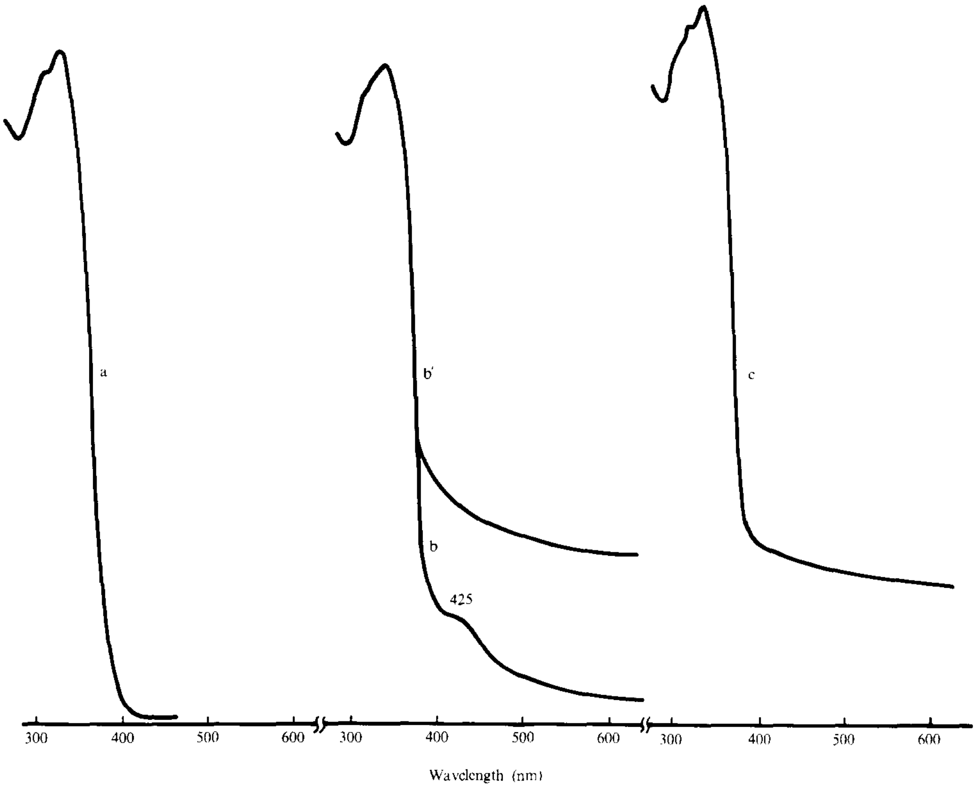

Fig. 5. UV–visible diffuse reflectance spectra: (a) raw TiO_2; (b) $(PtO_2+Pt(OH)_2)/TiO_2$; (b′) (b) treated at 230 °C in pure N_2 for 30 min; (c) $Pt(OH)_2/TiO_2$.

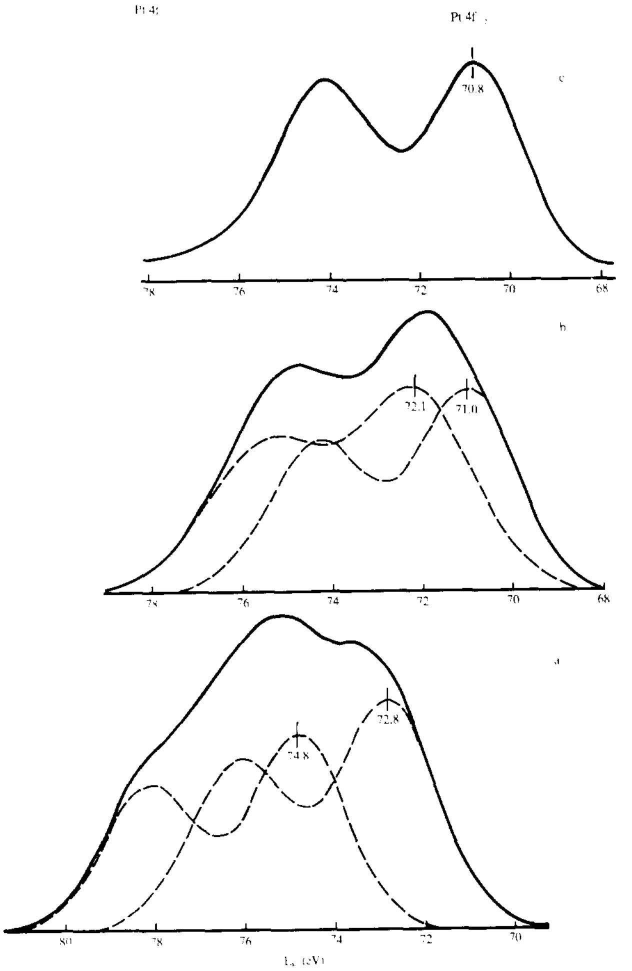

Fig. 6. XPS after heating in ultrahigh vacuum chamber: (a) room temperature; (b) 220 ± 10 °C for 30 min; (c) 620 ± 10 °C for 30 min.

reduction of $PtCl_6^{2-}$ in isopropyl alcohol (90 vol.%) solution. It was found that there was no Pt^0 formation until 90% of the Pt^{4+} species had been converted into Pt^{2+}, and it was concluded that Pt^{4+} inhibited its own reduction to Pt^0. However, in the microheterogeneous system, the hydrolysate of $PtCl_6^{2-}$ was converted to a solid deposit, $Pt(OH)_2$, on the surface of the semiconductor after receiving two photogenerated e^- and the reduction process was thus terminated.

If the pH value of the dispersion is below pH 12, no PtO_2 is deposited on the TiO_2 surface and the amount of Pt deposited decreases (Fig. 7). This results from the fact that $PtCl_6^{2-}$ hydrolysis decreases with increasing H^+ concentration. When the curve of Fig. 7 is extrapolated to pH → 0, the amount of Pt deposited on the surface will be close to zero, indicating that no photocatalytic conversion of the $PtCl_6^{2-}$ hydrolysate takes place on the TiO_2 surface. This deduction is in accord with the result given in the literature [2] (pH 0; deposition rate of Pt, 0.0 μmol h^{-1}).

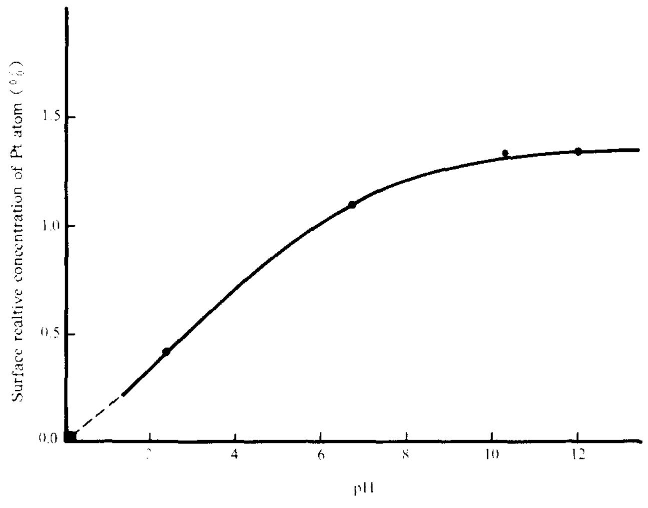

Fig. 7. Dependence of surface relative concentration of Pt atoms on pH value (● pH 2.32, [NaCl] = 0.28 M, corresponding to the point where this curve is extrapolated to pH 0).

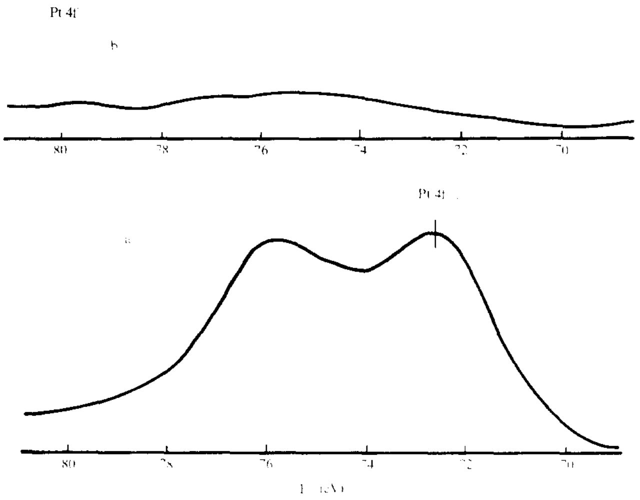

Fig. 8. Effect of Cl^- on photodeposit: (a) pH 12, [NaCl] = 0.28 M; (b) pH 2.3, [NaCl] = 0.28 M.

3.2. Effect of Cl^-

NaCl (0.32 g) was added to the dispersion used for test 1 (corresponding to [NaCl] = 0.28 M, about 55 times the initial [H_2PtCl_6]). After illumination, only $Pt(OH)_2$ was obtained on the TiO_2 surface (Fig. 8(a), Table 3, test 4). It has been shown that the Cl^- ions in an aqueous TiO_2 dispersion do not consume the photogenerated h^+ [18]; i.e., the following reaction does not happen:

$$2Cl^- + 2h^+ \xrightarrow{TiO_2} Cl_2 \qquad (8)$$

The function of a large amount of Cl^- is the same as that of increasing H^+ concentration (see Eq. (3)) so that there is no formation of PtO_2.

NaCl (0.32 g) was added to the dispersion used for test 3. After illumination, the amount of Pt deposited

Table 3
Effect of Cl^- and CH_3COOH on the photoconversion of $PtCl_6^{2-}$ in an aqueous TiO_2 dispersion

Test	pH (before illumination)	Initial $[H_2PtCl_6]$ (M)(	$[Cl^-]$ or $[CH_3COOH]$ (M)	Illumination time (h)	Photodeposit	Relative surface Pt concentration (%)
4	12.06	5.1×10^{-3}	$0.28(Cl^-)$	5	$Pt(OH)_2$	0.5
5	2.32	5.1×10^{-3}	$0.28(Cl^-)$	5	None [a]	–
6	12.16	5.1×10^{-3}	$0.1(CH_3COOH)($	5	$Pt(OH)_2$	1.5
7	3.93	5.1×10^{-3}	$0.1(CH_3COOH)$	5	Pt^0	0.8

[a] TiO_2 powder did not change colour after washing and drying.

on the TiO_2 surface was close to zero (Fig. 8(b), Table 3, test 5). This result indicates the following: (a) the hydrolysis of $PtCl_6^{2-}$ is inhibited completely by the joint effect of Cl^- and H^+; (b) as deduced above, no photocatalytic reaction of $PtCl_6^{2-}$ takes place on the TiO_2 surface.

The inhibitory effect of Cl^- on the hydrolysis of $PtCl_6^{2-}$ can also be ascertained from the absorption spectra shown in Fig. 9. A freshly prepared aqueous solution of $PtCl_6^{2-}$ (7.7×10^{-4} M, pH 2.56) gave three absorption bands ($\lambda = 445$ nm of ${}^1A_{1g}\rightarrow{}^3T_{1g}$ transition, $\lambda = 360$ nm of ${}^1A_{1g}\rightarrow{}^1T_{1g}$ transition and $\lambda = 260$ nm of ${}^1A_{1g}\rightarrow b^1T_{1u}$ transition) [10,11,19,20]. $\lambda = 205$–225 nm is the absorption of the $PtCl_6^{2-}$ hydrolysate (see Fig. 9(a)). After keeping this sample in the dark for 1 month, the three absorption bands disappear, while that of the hydrolysate remains (Fig. 9(b)). When 0.32 g of NaCl was added to the sample used in Fig. 9(a) and the solution was kept in the dark for 2 months, the positions of the absorptions did not change (Fig. 9(c)). This is due to the inhibitory effect of Cl^- on the hydrolysis of $PtCl_6^{2-}$.

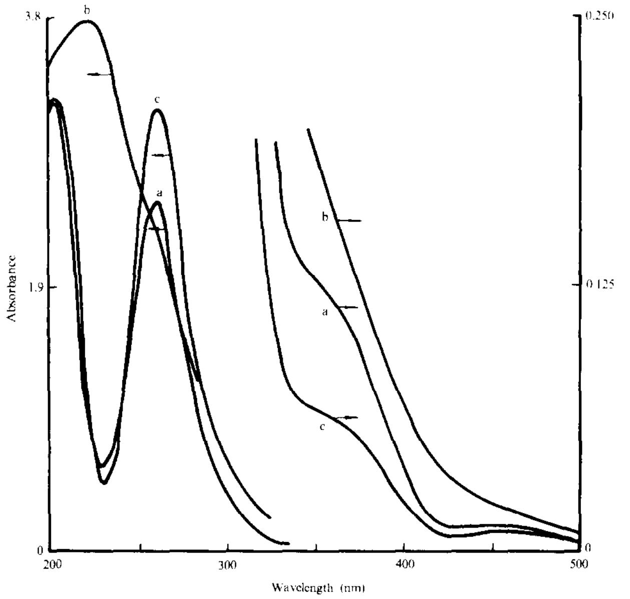

Fig. 9. Absorption spectra of aqueous H_2PtCl_6 (pH 2.56, initial $[H_2PtCl_6] = 7.7\times10^{-4}$ M): (a) determined immediately; (b) after keeping in the dark for 1 month; (c) added 0.32 g NaCl, after keeping in the dark for 2 months.

3.3. *Effect of CH_3COOH*

H_2PtCl_6 (0.077 M) and TiO_2 were added to 0.1 M CH_3COOH solution (pH 2.48) and the pH value was adjusted to pH 3.93 with concentrated NaOH; the dispersion was illuminated. The deposit formed on the TiO_2 surface was Pt^0 (Fig. 10(a), test 7 in Table 3). When the pH value of the dispersion was adjusted to pH 12 and then illuminated, only $Pt(OH)_2$ was found on the TiO_2 surface (Fig. 10(b)).

Acetic acid is a weak acid with $K_a = 1.85\times10^{-5}$. The degree of ionization of 0.1 M CH_3COOH at different pH values is given in Table 4. At pH 4, 84.7% of CH_3COOH is unionized; at pH 12, nearly all the CH_3COOH molecules are converted to CH_3COO^- ions. Recently, Kaise et al. [21] observed directly the free radical intermediates $^{\cdot}CH_2COOH$ and $^{\cdot}CH_3$ but not

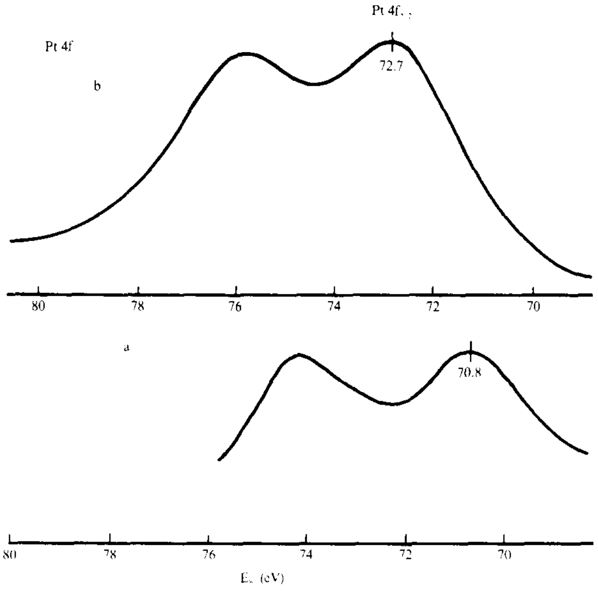

Fig. 10. Effect of CH_3COOH on photodeposit: (a) pH 3.9, $[CH_3COOH] = 0.1$ M; (b) pH 12.2, $[CH_3COOH] = 0.1$ M.

Table 4
Degree of ionization of 0.1 M CH_3COOH

pH	H^+ (M)	CH_3COO^-	Degree of ionization (%)
3	10^{-3}	0.177×10^{-2}	1.77
4	10^{-4}	1.53×10^{-2}	15.3
7	10^{-7}	9.94×10^{-2}	99.4
12	10^{-12}	≈ 0.1	≈ 100

$CH_3CO_2^{\cdot}$ using electron spin resonance (ESR) during illumination of a 0.1 M CH_3COOH dispersion of Pt^0/TiO_2 (pH $\approx$ 2.9). They suggested that CH_3COO^- accepts one h^+ to form directly $^{\cdot}CH_3$ and CO_2 (Eq. (1), Kolbe photoreaction), followed by hydrogen abstraction to form $^{\cdot}CH_2COOH$

$$^{\cdot}CH_3 + CH_3COOH \longrightarrow CH_4 + {}^{\cdot}CH_2COOH \qquad (9)$$

This is an interesting discovery which can help us to clarify the mechanism of Pt^0 formation in test 7. Since $^{\cdot}CH_2COOH$ is a reductive free radical [22], it may be possible that Pt^0 is formed through the reduction of $Pt(OH)_xCl_{6-x}{}^{2-}$ by $^{\cdot}CH_2COOH$ rather than the photogenerated e^- on the TiO_2 surface.

At pH 12, there will be no reaction according to Eq. (9), so that Pt^0 does not exist in the photodeposit of test 6. Although the presence of CH_3COO^- has no effect on $PtCl_6{}^{2-}$ hydrolysis, it can be a competitor for the consumption of the photogenerated h^+. If the reaction rate of Eq. (1) is more rapid than that of Eq. (6), the formation of PtO_2 will be inhibited. This is the probable reason why there was no PtO_2 in the deposit on the TiO_2 surface at pH 12.

4. Conclusions

(1) In an aqueous TiO_2 dispersion, $PtCl_6{}^{2-}$ is photocatalytically converted into a solid product via its hydrolysate.
(2) The degree of $PtCl_6{}^{2-}$ hydrolysis varies with the H^+ and Cl^- concentration in the dispersion. The composition and quantity of the photodeposits obtained on the TiO_2 surface depend on the degree of hydrolysis.
(3) When the concentration of H^+ and/or Cl^- is sufficiently high to inhibit the hydrolysis of $PtCl_6{}^{2-}$, no photodeposit is observed on the TiO_2 surface.
(4) The effect of CH_3COOH on the photocatalytic process of $PtCl_6{}^{2-}$ in a TiO_2 dispersion is closely related to the degree of ionization of CH_3COOH and the mechanism of the photo-Kolbe reaction.

Acknowledgements

This research was supported by the Gansu Province Natural Science Foundation. We also express our deep gratitude to Professor Linghui Tong and Zilu Liu for carrying out the UV–visible absorption, DSC and TGA determinations.

References

[1] B. Kraeutler and A.J. Bard, *J. Am. Chem. Soc.*, *100* (1978) 4317.
[2] W.W. Dunn and A.J. Bard, *Nouv. J. Chim.*, 5 (1981) 651.
[3] Y. Chen, Z. Wei, H. Liu and Y.X. Chen, *Cuihua Xuebao* (*J. Catal.*, in Chinese), *2* (1981) 194.
[4] A. Mill and G. Porter, *J. Chem. Soc., Faraday Trans. I*, *789* (1981) 3659.
[5] S. Sato, *J. Phys. Chem.*, *87* (1983) 3659.
[6] K. Yamaguti and S. Sato, *J. Phys. Chem.*, *89* (1985) 5510.
[7] J.S. Curran, J. Domenech, N. Jaffrezic-Renault and R. Philippe, *J. Phys. Chem.*, *89* (1985) 957.
[8] M. Koudelka, J. Sanchez and J. Augustynski, *J. Phys. Chem.*, *86* (1982) 4277.
[9] E. Blasius, W. Preetz and R. Schmilt, *J. Inorg. Nucl. Chem.*, *19* (1961) 115.
[10] L. Cox, D.G. Peters and E.L. Wehry, *J. Inorg. Nucl. Chem.*, *34* (1972) 297.
[11] Z. Jin, Z. Chen, Q. Li, C. Xi and X. Zheng, *J. Photochem. Photobiol. A: Chem.*, *81* (1994) 177.
[12] J.S. Hammond and N. Winograd, *J. Electroanal. Chem.*, *78* (1977) 55.
[13] G.C. Allen and P.M. Tucker, *J. Electroanal. Chem. Interfacial Electrochem.*, *50* (1974) 335
[14] T. Wang, A. Vazquez, A. Kato and L.D. Schmidt, *J. Catal.*, *78* (1982) 306.
[15] K.S. Kim, N. Winograd and R.E. Dairs, *J. Am. Chem. Soc.*, *93* (1971) 6296.
[16] R.C. Weast, *Handbook of Chemistry and Physics*, CRC Press, 79th edn., 1989–1990.
[17] R.E. Cameron and A.B. Bocarsly, *Inorg. Chem.*, *25* (1986) 2910.
[18] J.-M. Herrmann and P. Pichat, *J. Chem. Soc., Faraday Trans. I*, *76* (1980) 1138.
[19] D.L. Swihart and W.R. Mason, *Inorg. Chem.*, *9* (1970) 1749.
[20] C.M. Davidson and R.F. Jameson, *Trans. Faraday Soc.*, *61* (1965) 2462.
[21] M. Kaise, H. Kondoh, C. Nishihara, H. Nozoye, H. Shindo, S. Nimura and O. Kikuchi, *J. Chem. Soc., Chem. Commun.*, *4* (1993) 395.
[22] V.J. Lilie, G. Beck and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, *75* (1971) 458.