

## Effect of Surface Hydroxyl Groups of Pure TiO<sub>2</sub> and Modified TiO<sub>2</sub> on the Photocatalytic Oxidation of Aqueous Cyanide

Jae-Hyun Kim and Ho-In Lee<sup>†</sup>

School of Chemical Engineering & Research Center for Energy Conversion and Storage,  
Seoul National University, Seoul 151-744, Korea

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**Abstract**—It is still debatable whether the photocatalytic oxidation of cyanide proceeds via hydroxyl radicals or by photogenerated holes. We synthesized pure TiO<sub>2</sub> catalysts via sol-gel process. In order to elucidate the oxidation pathway of cyanide, we used hydroxyl radical scavengers and controlled the concentration of surface hydroxyl group on the catalysts adopting fluoride-exchange. The degree of fluoride-exchange of TiO<sub>2</sub> catalysts was independent of the pH of suspension. We also adopted a polyoxometalate, tungstophosphoric acid (TPA, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) which is well known for high charge transfer ability and hydrolytic stability. TPA-modified TiO<sub>2</sub> catalysts were prepared with sol-gel technique to overcome the high solubility of TPA in water. As another attempt for the insoluble TPA, proton of TPA supported on TiO<sub>2</sub> catalysts was replaced by cesium ion to form Cs-TPA/TiO<sub>2</sub> catalysts. Both attempts were successful in immobilizing TPA on TiO<sub>2</sub> catalysts. Commercially available TiO<sub>2</sub> catalysts such as P25 from Degussa AG were also used as catalysts. XRD analysis revealed that pure TiO<sub>2</sub> and TPA-modified TiO<sub>2</sub> catalysts prepared by sol-gel process were composed of well-developed anatase crystalline structure. In the presence of hydroxyl radical scavengers, the photoactivity of TPA-modified TiO<sub>2</sub> catalysts was retarded much less than that of pure TiO<sub>2</sub> catalysts. The concentration of surface hydroxyl group was effectively suppressed by the fluoride-exchange causing the decrease of the activity of the catalysts. In the case of fluoride-exchanged catalysts, the drop in activity was obvious for the pure TiO<sub>2</sub> catalysts in the presence of iodide as a hydroxyl radical scavenger suggesting that indirect oxidation via hydroxyl radicals was the preferential reaction pathway. For the TPA-modified TiO<sub>2</sub> catalysts, meanwhile, the diminution was such a small extent suggesting that direct oxidation by photogenerated holes was the main reaction pathway. The activity arising from TPA in the catalysts was due to the Keggin structured anion (PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>) which acted as an electron relay with the aid of dissolved oxygen in the reaction system.

**Key words:** Cyanide, Oxidation Pathway, Surface Hydroxyl Group, Tungstophosphoric Acid

### INTRODUCTION

The presence of free and complex cyanides in industrial effluents is a problem of major concern because of the infamous toxicity of these species to ecosystems. Cyanide has been used as the unparalleled leaching agent for the extraction of gold from ore. Harmful industrial aqueous wastes containing free and complex cyanides are generated in a great amount from refining, electroplating, and heat-treating of gold as well as coal gasification process. There have been conventional treatment processes including physical, chemical, and biological methods to remove free and complex cyanides dissolved in water. Physical treatments include ion exchange, adsorption by activated carbon, flotation-foam separation, reverse osmosis, and electrodialysis. Biological methods are based on biodegradation. Chemical processes involve alkaline chlorination which is currently the best reliable technique, the INCO process using SO<sub>2</sub>-air, the Degussa process using hydrogen peroxide, electrolytic decomposition, and the oxidation of cyanide by oxidants such as ferrate (VI), ozone, and permanganate. These methods, however, are not free from some drawbacks. For instance, in the physical treat-

ments, cyanides are not decomposed or treated but only shifted from water to another phase. For the biological methods, the reaction rate is so low that the method is limited to low concentrations of cyanides. And, in the chemical processes, oxidants are generally expensive and some metal cyanide complexes are not decomposed by the chemical oxidation. Especially, for alkaline chlorination, highly toxic cyanogen chloride (CNCl) is produced [Futakawa et al., 1994; Wu et al., 1998; Alicilar et al., 2002].

Oxidation and/or mineralization of organic and inorganic pollutants in water by photocatalytic oxidation process has been attractive as a promising alternative to the existing treatment techniques because of many advantages as follows [Mills and Le Hunte, 1997; Fujishima et al., 2000; Lee et al., 2001; Pirkanniemi and Sillanpää, 2002]: (1) semiconductors used as photocatalysts are stable in a wide range of pH (0 ≤ pH ≤ 14) of aqueous solutions, (2) semiconductor powders are cheap in price, (3) no additives except air are needed, (4) photocatalytic activity is rarely interfered by ionic species frequently present in water, and (5) this technique can be combined with another treatment process such as biological methods.

In photocatalytic oxidation, photogenerated holes on the surface of a semiconductor particle when the particle absorbs light energy higher than its band gap energy are used as an oxidant presumably as a form of hydroxyl radicals. Photocatalytic oxidation, in this respect, is a member of advanced oxidation processes (AOP) [Gao et al., 2002; Hong et al., 2002]. However, two oxidation pathways

<sup>†</sup>To whom correspondence should be addressed.

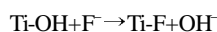
E-mail: hilee@snu.ac.kr

<sup>‡</sup>This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

are possible in photocatalytic oxidation: (1) oxidation via hydroxyl radicals and (2) oxidation by photogenerated holes. Meanwhile, electrons must be efficiently removed in order to enhance the photocatalytic activity, otherwise recombination between holes and electrons would promptly decrease the activity to a great extent. Molecular oxygen dissolved in water acts as an electron scavenger leading to superoxide radicals to sufficiently meet the need [Konovalova et al., 1999].

Photocatalytic oxidation of cyanides is presented elsewhere [Kim and Lee, 2003; Chiang et al., 2002; Hernández-Alonso et al., 2002; Kim et al., 2001; Frank and Bard, 1977]. Cyanate and nitrate are reported to be produced, but the distribution of the products depends on experimental conditions. It is still ambiguous whether the photocatalytic oxidation of cyanide proceeds via hydroxyl radicals or by photogenerated holes.

In this study, we made an effort to elucidate the photocatalytic oxidation pathways of cyanide in water. To do this, we modulated the concentration of surface hydroxyl groups on the catalysts using fluoride-exchange reaction. Fluoride shows strong adsorption ability on TiO<sub>2</sub>. Fluoride ions replace surface hydroxyl groups on TiO<sub>2</sub> according to the following equation [Minero et al., 2000].



Because hydroxyl radicals are accepted to be formed from the reactions between photogenerated holes and surface hydroxyl groups and/or water molecules adsorbed on TiO<sub>2</sub>, we could reduce the portion of hydroxyl radicals in the cyanide oxidation by suppressing surface hydroxyl groups on the catalysts with the fluoride-exchange reaction. Hydroxyl radical scavengers were also utilized for this purpose. We adopted a polyoxometalate, tungstophosphoric acid (TPA, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) which is well known for high charge transfer ability and hydrolytic stability [Kozhevnikov, 1998; Hiskia et al., 2001]. Therefore, pure TiO<sub>2</sub> catalysts and TPA-modified TiO<sub>2</sub> catalysts were prepared for the experiments. Despite the excellent redox property, TPA is very soluble in water. To keep the catalytic system heterogeneous throughout the experiments, TPA must be insoluble in the aqueous environment. There are two attempts for the preparation of insoluble TPA to be considered [Guo et al., 2002; Choi et al., 2000]: (1) immobilization or incorporation of TPA into the solid matrix, and (2) preparation of insoluble TPA salt by substitution of cations. We tried both attempts, that is, (1) TPA was incorporated into TiO<sub>2</sub> framework via a sol-gel technique and (2) proton of TPA supported on TiO<sub>2</sub> was replaced by cesium ion to form Cs-TPA/TiO<sub>2</sub>.

## EXPERIMENTAL

### 1. Preparation of Catalysts

TPA-modified TiO<sub>2</sub> and pure TiO<sub>2</sub> catalysts were synthesized as follows: 0.051 g of TPA (Kanto Chemical Co., Inc., GR grade) corresponding to 1 wt% was dissolved in the mixture of 112.5 mL of water and 20 mL of isopropyl alcohol (IPA; Daejung Chemicals & Metals Co., Ltd., EP grade), and 18.3 mL of titanium tetraisopropoxide (TTIP; Junsei Chemical Co., Ltd., GR grade) was mixed with 20 mL of IPA. The latter was added dropwise into the former. To make sure the effect of the hydrolysis environment during sol-gel process on the catalytic activity, the former was reversely done

into the latter. After the treatment mentioned below, catalysts SG-1 and SG-2 were obtained, respectively. On the other hand, catalysts SG-3 and SG-4 were obtained by using the above aqueous solution without TPA following the same preparation method of SG-1 and SG-2, respectively. Treatment procedure was as follows: Aging for 6 h was followed by drying at 110 °C for 12 h and then calcining at 300 °C for 2 h.

Commercially available TiO<sub>2</sub> was also used as catalyst, that is, anatase and rutile TiO<sub>2</sub> from Aldrich Chemical Co., Inc. (abbreviated as 'Ana' and 'Rut', respectively) and P25 from Degussa AG were utilized as purchased.

The procedure to prepare fluoride-exchanged TPA-modified TiO<sub>2</sub> and TiO<sub>2</sub> catalysts was as follows: 0.525 g of NaF (Samchun Pure Chemical Co., Ltd., GR grade) was dissolved into 200 mL of water followed by adding 5 g of TiO<sub>2</sub> into the solution. The resultant suspension contained a fluoride concentration of  $6.25 \times 10^{-2}$  mol L<sup>-1</sup>. The pH of the suspension was then adjusted to 3.5 by the addition of concentrated nitric acid (Daejung Chemicals & Metals Co., Ltd., 60%, EP grade) according to Minero et al. [2000]. For comparison, the same suspension was prepared except that the pH of the suspension was not adjusted deliberately, and the value was measured to be 6.2. The suspensions were mixed well with a magnetic stirrer at room temperature for 12 h to allow ion exchange to be completed. The TiO<sub>2</sub> particles in each suspension were retrieved by vacuum filtration. The ion-exchanged TiO<sub>2</sub> samples were dried in an oven at 110 °C for 24 h and finally calcined at 300 °C for 2 h.

Cs-exchange reactions of TPA-modified TiO<sub>2</sub> catalysts using a two-step (sequential) impregnation method were performed. In the first step, CsOH (Kanto Chemical Co., Inc., GR grade) was impregnated by aqueous incipient wetness onto TiO<sub>2</sub> and dried at 110 °C for 24 h. Following this, TPA was impregnated by using a similar aqueous incipient wetness technique, dried at 110 °C for 24 h and calcined at 300 °C for 2 h.

IPA, acetone (Aldrich Chemical Co., Inc., HPLC grade), bromide (KBr; Merck, IR grade), and iodide (KI; Mallinckrodt Chemical Works, GR grade) were used as hydroxyl radical scavengers as purchased without further purification.

### 2. Photocatalytic Activity Tests

A biannular Pyrex glass batch reactor with a lamp immersed in the inner part was used for all the photocatalytic experiments. The volume of the reactor was 300 mL and 200 mg of catalyst was added for each test. Magnetic stirring maintained both concentration and temperature of the suspension uniform throughout the experiments. The initial concentration of cyanide was adjusted to ca. 1.9 mmol L<sup>-1</sup> (corresponding to 50 mg L<sup>-1</sup>) using KCN (Fluka AG, GR grade). N<sub>2</sub> and O<sub>2</sub> were used to regulate the concentration of dissolved oxygen in the suspension during irradiation. The suspension was illuminated by a 450 W high pressure Hg lamp (Kumkang Industrial Co.). A Pyrex glass thimble surrounding the lamp removed any radiation whose wavelength was below 300 nm, and the circulation of distilled water in the thimble was allowed to cool the lamp and to withdraw the IR fraction of the beam. Incident light intensity was measured by ferrioxalate actinometry [Calvert and Pitts, 1966] and was determined to be  $8.66 \times 10^{-3}$  einstein s<sup>-1</sup>.

The concentration of cyanide was measured with standard silver nitrate titration method [Clesceri et al., 1998]. Identification and quantification of products such as cyanate, nitrite, and nitrate were

performed by an ion chromatograph (DX 120, Dionex) equipped with an anion-exchange column (IonPac AS14A).

In order to make sure the charge transfer ability of TPA, homogeneous photo-reaction system which included cyanide and TPA dissolved in water without  $\text{TiO}_2$  was adopted.

### 3. Characterization of Catalysts

FT-IR spectroscopic analysis (Prospect IR, Midac Corp.) was conducted for the determination of surface hydroxyl groups of the catalysts. Pellets of 12 mm in diameter for this experiment were prepared by adding the sample to KBr powder.

UV-Vis absorbance (UV-2401PC, Shimadzu Corp.) was measured for the quantitative determination of the concentration of  $\text{PW}_{12}\text{O}_{40}^{3-}$ , the Keggin anion of TPA eluted from the catalysts during the photo-activity tests and  $\text{PW}_{12}\text{O}_{40}^{4-}$ , the reduced form of the Keggin anion in the homogeneous reaction.

Powder X-ray diffraction analysis (M18XHF22-SRA, Mac Science Co.) was performed for the information of crystalline structures of the catalysts using Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ).

BET specific surface areas of the catalysts were measured by using  $\text{N}_2$  adsorption technique (ASAP 2010, Micromeritics).

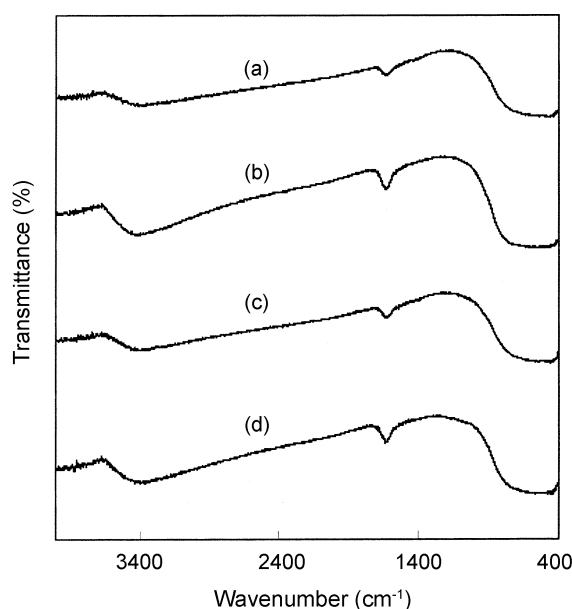
## RESULTS AND DISCUSSION

As an attempt to eliminate the portion of hydroxyl radicals on the surface of catalysts in photocatalytic activity, several hydroxyl radical scavengers were used during the photocatalytic oxidation of cyanide. Meanwhile, in our previous study, the photocatalytic oxidation of cyanide followed zeroth order kinetics when the concentration of dissolved oxygen in the reaction mixture remained constant during irradiation [Kim and Lee, 2003]. Therefore, the activities of the catalysts were expressed by the reaction rate constant calculated on the basis of zeroth order kinetics. In the presence of hydroxyl radical scavengers, in Table 1, the photoactivity of TPA-modified  $\text{TiO}_2$  catalysts (SG-1 and SG-2) was retarded less than that of pure  $\text{TiO}_2$  catalysts (SG-3 and SG-4). It suggests that the pure  $\text{TiO}_2$  catalysts were more dependent on hydroxyl radicals in the photocatalytic activity than the TPA-modified  $\text{TiO}_2$  catalysts. Among the hydroxyl radical scavengers used, iodide was the most powerful one, and was chosen as the scavenger for the rest of experiments in this study accordingly.

The activities of catalysts SG-2 and SG-4 were higher than those of catalysts SG-1 and SG-3, respectively, for all cases irrespective of the presence of hydroxyl radical scavengers, and moreover, all the catalysts showed activities comparable to P25 whose activity was  $4.90 \times 10^{-5} \text{ M min}^{-1}$  in the absence of any hydroxyl radical scavenger.

**Table 1. Effect of hydroxyl radical scavenger on the photocatalytic oxidation of cyanide (Concentrations of scavengers were fixed at  $800 \mu\text{mol L}^{-1}$ ; activity in  $10^{-5} \text{ M min}^{-1}$ )**

	SG-1	SG-2	SG-3	SG-4
No scavenger	4.93	5.20	4.71	4.95
Isopropyl alcohol	3.95	4.11	1.88	1.95
Acetone	4.11	4.40	2.15	2.33
Bromide	3.83	4.02	1.43	1.49
Iodide	3.60	3.69	0.73	0.77



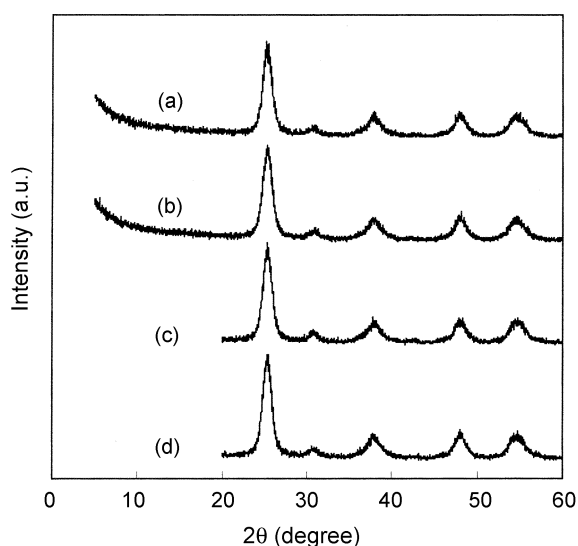
**Fig. 1. FT-IR spectra of catalysts: (a) SG-1, (b) SG-2, (c) SG-3, and (d) SG-4.**

Hydroxyl radicals on the surface of catalysts could be formed from surface hydroxyl groups at which photogenerated holes could be trapped. The hydroxyl radicals could also arise from the reaction between photogenerated holes and adsorbed water molecules in the reaction system. In order to find the relationship between the photoactivity and the surface hydroxyl groups of catalysts, FT-IR spectra of the catalysts were obtained. In Fig. 1, the FT-IR spectra of the catalysts showed a broad band in the region of  $3,700\text{--}2,500 \text{ cm}^{-1}$  (O-H stretching) with a maximum at  $3,420 \text{ cm}^{-1}$ . Another peak at  $1,630 \text{ cm}^{-1}$  (H-O-H bending from adsorbed water molecules) was also shown. The peak area of OH stretching was indicative of the amount of the surface hydroxyl group of the catalyst. The peak areas of the OH stretching of catalysts SG-2 and SG-4 were larger than those of catalysts SG-1 and SG-3, respectively. The peak areas of the surface hydroxyl groups of SG catalysts were calculated out of absorbance spectra converted from the transmittance ones of FT-IR shown in Fig. 1. The results obtained are given in Table 2, and the relative amounts of the surface hydroxyl groups of the catalysts were normalized to SG-2 as follows: SG-1 : SG-2 : SG-3 : SG-4 = 0.51 : 1.00 : 0.60 : 0.85. The synthetic method for catalysts SG-2 and SG-4 made the textural property of the catalysts more favorable to the photocatalytic oxidation of cyanide, that is, catalysts SG-2 and SG-4 possessed much higher concentration of surface hydroxyl groups than catalysts SG-1 and SG-3, respectively. In the meantime, for catalysts SG-1 and SG-2, no peaks characteristic of TPA occurring at  $1,080 \text{ cm}^{-1}$  (P-O str.),  $980 \text{ cm}^{-1}$  (W=O str.),  $890 \text{ cm}^{-1}$  (corner-sharing W-O-W str.), and  $800 \text{ cm}^{-1}$  (edge-sharing W-O-W str.) were observed because of the small loading of TPA (corresponding to 1 wt%). The characteristic peaks for TPA in FT-IR spectra were observed as the loading of TPA was increased up to 30 wt%.

Other physical properties of the SG catalysts such as crystalline structures and specific surface areas were analyzed. As shown in Fig. 2, it was revealed from XRD analysis that pure  $\text{TiO}_2$  and TPA-

**Table 2. Primary crystallite size, specific surface area, relative amount of surface hydroxyl group, and surface area-normalized surface hydroxyl group density of SG and P25 catalysts**

	Crystallite size (Å)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Relative amount of surface hydroxyl group	Surface area-normalized surface hydroxyl group density
SG-1	79	162	51.2	0.544
SG-2	75	172	100	1.00
SG-3	82	156	60.4	0.666
SG-4	77	168	85.1	0.873
P25	284	50	67.5	2.32

**Fig. 2. XRD patterns of catalysts: (a) SG-1, (b) SG-2, (c) SG-3, and (d) SG-4.**

modified TiO<sub>2</sub> catalysts prepared by sol-gel reaction were composed of well-developed anatase crystalline structure although the calcination temperature was limited to 300 °C taking into consideration that TPA decomposes thermally at ca. 450 °C.

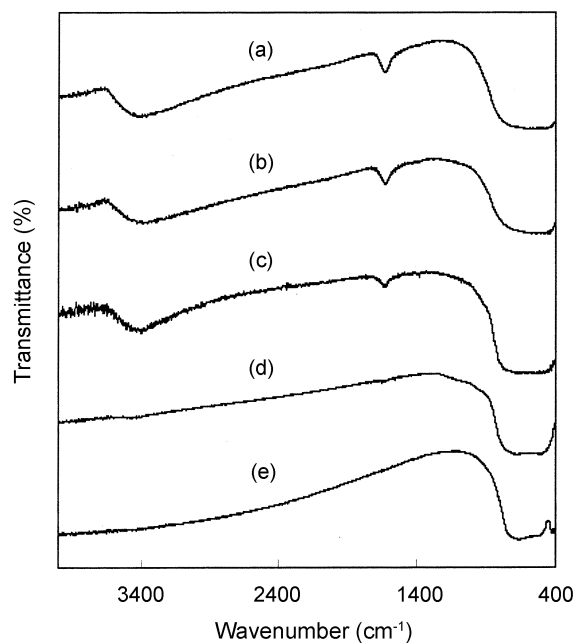
Two major peaks ( $2\theta=25.3^\circ$  and  $10.2^\circ$ ) of TPA were not observed for catalysts SG-1 and SG-2. The peak at  $2\theta=25.3^\circ$  might be superimposed by the (110) plane of anatase TiO<sub>2</sub>; however, the peak at  $2\theta=10.2^\circ$  was not shown yet. It suggests that TPA was well dispersed in the framework of TiO<sub>2</sub> during the sol-gel process. When the loading of TPA was increased up to 30 wt%, the characteristic peaks in XRD patterns were clearly observed. Primary crystallite sizes were derived from the XRD peak ( $2\theta=25.3^\circ$ ) for anatase (110) plane in Fig. 2 using the Scherrer equation. The crystallite sizes of SG-2 and SG-4 were smaller than those of SG-1 and SG-3, respectively (Table 2). This presumably brought about the difference in the specific surface areas of the catalysts, which was related to the amount of the surface hydroxyl groups of the catalysts shown in Fig. 1.

As mentioned earlier, the difference in the synthetic method for the SG catalysts was the main factor which resulted in the differences in the specific surface areas and especially the amount of the surface hydroxyl groups of the catalysts. Meanwhile, in Table 2, the specific surface area of catalyst P25 was much smaller than that of SG catalysts although the photoactivity of the catalyst was comparable to that of SG catalysts. Such a high photoactivity of the cat-

**Table 3. Effect of fluoride-exchange of catalyst on the photocatalytic oxidation of cyanide**

	N. C.* (10 <sup>-5</sup> M min <sup>-1</sup> )	Fluoride-exchange at pH 3.5 (10 <sup>-5</sup> M min <sup>-1</sup> )	Exchanged fluoride (mol g-cat <sup>-1</sup> )
SG-2	5.20	4.35	$3.2 \times 10^{-4}$
Cs-TPA/Ana	2.65	2.57	$7.0 \times 10^{-6}$
Cs-TPA/Rut	2.40	2.39	$1.3 \times 10^{-6}$
SG-4	4.95	3.06	$2.4 \times 10^{-4}$
Ana	2.39	2.35	$7.1 \times 10^{-6}$
Rut	2.12	2.10	$1.3 \times 10^{-6}$
P25	4.90	2.52	$2.3 \times 10^{-4}$

\*not changed: no fluoride-exchange performed.

**Fig. 3. FT-IR spectra of catalysts: (a) SG-2, (b) SG-4, (c) P25, (d) Ana, and (e) Rut.**

alyst P25 could be ascribed to higher density of the surface hydroxyl group compared with SG catalysts.

In order to examine the effect of the surface hydroxyl group of the catalysts on the photoactivity in detail, we tried to reduce the absolute amount of the surface hydroxyl group by taking advantage of the fluoride-exchange reaction. Before the fluoride-exchange

reaction was performed, catalysts Ana and Rut showed poor activities compared with catalysts SG-2, SG-4, and P25 as shown in Table 3. Catalysts Ana and Rut containing TPA still exhibited poor activities although their activities were enhanced by the incorporation of TPA (Table 3). As shown in Fig. 3, catalysts Ana and Rut possessed negligible amount of the surface hydroxyl group compared with catalysts SG-2, SG-4, and P25. Such small amounts of surface hydroxyl group of the catalysts Ana and Rut were also evidenced by the small amounts of fluoride exchanged. The activities of catalysts SG-2, SG-4, and P25 were decreased when they experienced the fluoride-exchange reaction while those of catalysts Ana and Rut were almost unchanged. It suggests that in the case of  $\text{TiO}_2$  photocatalysts irrespective of the incorporation of TPA, the surface hydroxyl group played a significant role in the photocatalytic oxidation of cyanide.

It was thought that the activities of catalysts Ana and Rut arose from the surface hydroxyl radicals formed by the reaction between photogenerated holes and adsorbed water molecules in the reaction mixture.

From Fig. 4, the amount of the surface hydroxyl group of  $\text{TiO}_2$  (P25 in this case) was suppressed by ca. 80% during the fluoride-exchange. The remaining surface hydroxyl group (ca. 20% compared with the original amount) was thought to be the active sites of the catalysts SG-2, SG-4, and P25. In this study, the pH of the fluoride-containing solution had little impact on the degree of the fluoride-exchange, which is contrary to the literature [Minero et al., 2000]. The result was thought to be due to the sufficient aging time for 12 h during which the equilibrium of the exchange reaction could be reached.

From the results, we recognized that the adoption of either hydroxyl radical scavenger or fluoride-exchange was insufficient for disregarding the participation of hydroxyl radical on the catalyst surface in photo-oxidation of cyanide. Therefore, we adopted both hydroxyl radical scavenger and fluoride-exchange simultaneously

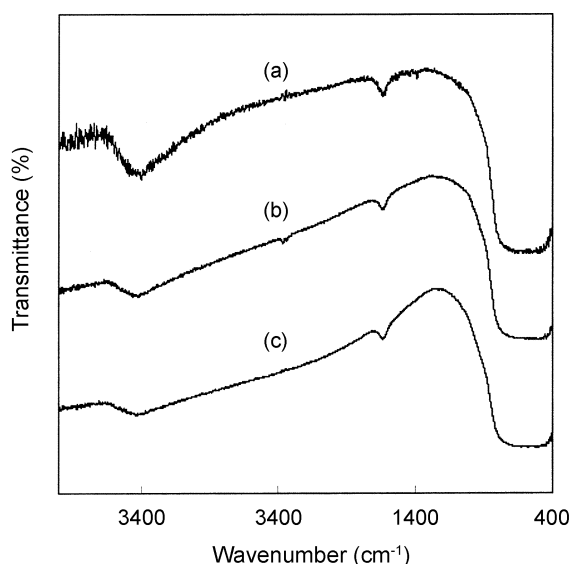


Fig. 4. FT-IR spectra of P25: (a) before fluoride-exchange, (b) after fluoride-exchange at pH 3.5, and (c) after fluoride-exchange at pH 6.2.

Table 4. Activities of fluoride-exchanged catalysts in the presence of iodide as hydroxyl radical scavenger (in  $10^{-5} \text{ M min}^{-1}$ )

	N. C.*	Fluoride-exchange at pH 3.5	Iodide as hydroxyl radical scavenger
SG-2	5.20	4.35	3.69
Cs-TPA/Ana	2.65	2.57	1.75
Cs-TPA/Rut	2.40	2.39	1.33
SG-4	4.95	3.06	0.77
Ana	2.39	2.35	0.50
Rut	2.12	2.10	0.38
P25	4.90	2.52	0.59

\*not changed: no fluoride-exchange performed & no hydroxyl radical scavenger added.

(Table 4). That is, the reaction system was composed of fluoride-exchanged catalyst suspended in aqueous solution with cyanide and iodide. As mentioned previously, iodide was used as the hydroxyl radical scavenger. In this case, pure  $\text{TiO}_2$  catalysts lost almost all the photoactivity. On the contrary, TPA-modified  $\text{TiO}_2$  catalysts still exhibited remarkable photoactivity. It suggests that for pure  $\text{TiO}_2$  catalysts, indirect oxidation via surface hydroxyl radical was the major pathway of the photo-oxidation of cyanide, whereas TPA-modified  $\text{TiO}_2$  catalysts presented another reaction pathway, that is, direct oxidation by photogenerated holes.

In order to find out the role of TPA in  $\text{TiO}_2$  catalysts, we tested the photoactivity of TPA dissolved in the reaction solution as a homogeneous photocatalyst. That is, the photocatalytic ability of TPA was observed from the homogeneous reaction system which included cyanide and TPA dissolved in water without  $\text{TiO}_2$  catalyst. TPA was active in oxidizing cyanide under illumination while it showed no activity under dark condition suggesting that TPA acted as a homogeneous photocatalyst. It was noteworthy that the homogeneous TPA was ca. 10 times more active than a heterogeneous  $\text{TiO}_2$  catalyst for the same molar amount of the two catalysts.

The result suggests that the enhancement of the photocatalytic activity of  $\text{TiO}_2$  is expected when doped with TPA on its surface. The TPA on  $\text{TiO}_2$  surface was a composite semiconductor system in which the desirable flow of photogenerated electrons and holes would lead to efficient separation of the two essential reactants. As shown in Table 5, the result was, however, opposite to the expectation. The photoactivity of catalyst P25 doped with cesium-exchanged

Table 5. Amounts of TPA eluted from catalysts with different loading of TPA during the photocatalytic oxidation of cyanide and the activities of Cs-TPA/P25 catalysts (The concentration of leached TPA was measured after 60 min of irradiation)

	TPA/P25 (mg L <sup>-1</sup> )	Cs-TPA/P25 (mg L <sup>-1</sup> )	Activity of Cs-TPA/P25 ( $10^{-5} \text{ M min}^{-1}$ )
1 wt%	1.2	N. D.*	5.23
3 wt%	5.7	N. D.	4.71
5 wt%	8.0	N. D.	4.63
10 wt%	32	N. D.	4.60

\*not detected.

TPA salt was decreased as the loading of TPA salt was increased from 1 wt% to 10 wt%. It suggests that the TPA doped on TiO<sub>2</sub> catalyst did not act as another photocatalyst.

Therefore, we turned to another role of TPA, that is, as an electron scavenger. Because of its high ability in charge transfer, TPA in TiO<sub>2</sub> would readily act as the electron scavenger resulting in the enhancement of the photoactivity of the catalysts. PW<sub>12</sub>O<sub>40</sub><sup>4-</sup>, the one-electron reduced Keggin anion of TPA, was observed with absorption maxima at around 750 nm and 485 nm, and it was promptly re-oxidized to PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> in the presence of dissolved oxygen in the homogeneous reaction system. The rate of re-oxidation was much slower (less than one tenth) when no dissolved oxygen acted as another electron scavenger. Therefore, it is thought that TPA in TiO<sub>2</sub> acted as the electron scavenger to convert Keggin anion to one-electron reduced form, and that it came back to its original oxidation state with the aid of dissolved oxygen which accepted electrons from the reduced TPA.

When it comes to the sol-gel method, TPA up to 1 wt% in loading was successfully localized in TiO<sub>2</sub> framework and the photoactivity reached a maximum at 1 wt% of TPA loading. When the amount of TPA exceeded the limit, all the TPA did not remain in the framework and a portion of TPA began to dissolve out from the catalysts during the oxidation of cyanide. That is the reason why the amount of TPA was fixed at 1 wt% for the TPA-modified TiO<sub>2</sub> synthesized by sol-gel technique. Up to 1 wt% loading, the TPA incorporated in TiO<sub>2</sub> framework exhibited a positive effect on the photoactivity, that is, catalysts SG-1 and SG-2 were more active than catalysts SG-3 and SG-4, respectively. Meanwhile, in Table 5, it was found that cesium-exchange gave insoluble TPA salt in TiO<sub>2</sub> successfully.

In order to make sure the effect of cesium in TPA salt on the photoactivity of catalysts, we prepared a series of TiO<sub>2</sub> catalysts containing cesium-exchanged TPA such as Cs/SG-2, Cs-TPA/SG-4, and Cs-TPA/P25. As shown in Table 6, no cesium effect was observed. We prepared TPA salt with ammonium ion as another cation instead of cesium, and no noticeable cation effect was observed, either.

## CONCLUSIONS

It is still debatable whether the photocatalytic oxidation of aqueous cyanide proceeds via hydroxyl radicals or by photogenerated holes. We adopted TPA in order to enhance the photoactivity of pure TiO<sub>2</sub> catalysts and elucidate the pathway of photo-oxidation of cyanide. In the case of TiO<sub>2</sub> photocatalysts, irrespective of the presence of TPA, the surface hydroxyl group played a significant role

in the photo-oxidation of cyanide. For pure TiO<sub>2</sub> catalysts, indirect oxidation via surface hydroxyl radical was the major pathway, whereas TPA-modified TiO<sub>2</sub> catalysts introduced another reaction pathway, that is, direct oxidation by photogenerated holes. The photoactivity of TPA-modified TiO<sub>2</sub> catalysts reached a maximum at 1 wt% of TPA loading. TPA in TiO<sub>2</sub> catalysts acted as the electron scavenger to convert Keggin anion to one-electron reduced form, and it returned to its original oxidation state with the aid of dissolved oxygen which accepted electrons from the reduced TPA.

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**Table 6. Effect of cesium in TPA-modified TiO<sub>2</sub> on the photocatalytic oxidation of cyanide (activity in 10<sup>-5</sup> M min<sup>-1</sup>)**

	N. C.*	Fluoride-exchange at pH 3.5	Iodide as hydroxyl radical scavenger
SG-2	5.20	4.35	3.69
Cs/SG-2	5.23	4.36	3.69
Cs-TPA/SG-4	5.20	4.25	3.50
Cs-TPA/P25	5.23	4.29	3.54

\*not changed: no fluoride-exchange performed & no hydroxyl radical scavenger added.

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