The Photodegradation of Surfactants. XVI.
Photocatalytic Effect of Various Semiconductors on the Photooxidation of Surfactants

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Effects of such n-type semiconductors as TiO2 (anatase, rutile or surface-modified TiO2 and Pt-loaded TiO2), ZnO, WO3 and MoS2 on the photodegradation of anionic DBS and cationic BDDAC surfactants, and related model compounds were examined in the present study. The anatase form of TiO2 showed greater photocatalytic activity than the rutile form. Noble-metal loaded catalysts (e.g., TiO2/Pt) were less photooxidative than the naked anatase TiO2 catalyst, possibly due to suppression of electron transfer of O2 to give O2—, namely photoreduction. The ZnO semiconductor catalyst decomposed DBS more rapidly than anatase TiO2. The photocatalytic activity of the other semiconductors examined (WO3 and MoS2) was only slight in each case.

Introduction

Environmental pollution by chemical materials is one of several serious problems which must be solved globally. It is very difficult to remediate contaminated sites containing large amounts of chemicals only by the bacterial biodegradation method of an activated sludge. Advanced oxidation technologies (AOT) such as UV/O3, UV/peroxide and photocatalysis, together with ozone treatment, high temperature-combustion, plasma procedure, alkaline or acidic hydrolysis, sonication or UV irradiation have all been investigated. However, to some extent these methods have some advantages and disadvantages. The photocatalytic degradation method that uses a TiO2 semiconductor catalyst has some attractive characteristics: (1) rapid decomposition, (2) non-selectivity, (3) complete mineralization (4) inexpensive (save energy) when using solar exposure, (5) non-toxic, and (6) the catalyst can be immobilized.

In the past few years, we have published extensively on the photodegradation of some toxic or carcinogenic chemicals: agrochemicals of pesticide or herbicide (permethrin)11,2), chlorinated compounds of DDT3, chlorinated compounds of DDT3, chloropheno14 and cyanide5). The detoxification or photomineralization by TiO2 catalyst is one of the more promising methods. Surfactants discharged from industrial and domestic activities are the predominant causes of aquatic pollution in rivers, lakes and seas. The authors have reported a series of studies concerning the photocatalytic degradation of surfactants by the TiO2 catalyst6–22). The effect of the nature of the n-semiconductor catalysts on the photodegradation of surfactants, however, has not been examined in detail.

This paper deals with the photodegradation of anionic and cationic surfactants and
some model compounds catalyzed by various types of n-semiconductors.

**Experimental details**

**Materials** The anionic materials of sodium dodecylbenzene sulfonate C_{12}H_{25}-C_6H_4-SO_3Na (DBS) and sodium benzene sulfonate C_6H_5-SO_3Na (BS) were supplied by Tokyo Kasei Co. Ltd. The cationic samples of benzyl tetradecyldimethyl ammonium chloride [C_6H_5-CH_2-N^+(CH_3)_2(C_{14}H_{29})] Cl^- (BTDAC), benzyl trimethyl ammonium chloride [C_6H_5-CH_2-N^+(CH_3)_3] Cl^- (BTAC) and dodecyl pyridinium chloride [C_{12}H_{25}-N^+ C_5H_5] Cl^- (C_{12}-PC) were commercial products from Wako Pure Chem. Ind. The TiO_2 catalyst employed was Degussa P-25 (ca. 80 % anatase and 20 % rutile) having an average particle size of about 30 nm (about 55 m^2 / g surface area). The TiO_2(P-25)/Pt (0.73%, 1 % and 1.5 %) catalysts were prepared by a procedure involving reduction of H_2PtCl_6 with citric acid in the reference^{23}. The rutile TiO_2 catalyst used was commercially available from Wako Pure Chem. Ind. The surface-modified TiO_2 catalyst was T-805 (Japan Aerosil Co. Ltd.) having a surface area of 30 ± 10 m^2 / g. The surface of T-805 was hydrophobic by modification of TiO_2 (P-25) particulates with octyltrimethyl silane. The ZnO photocatalyst supplied by Wako Pure Chem. Ind. is reagent grade (99.9 %) having an average particle size of ~5 μm. The n-type semiconductors WO_3 (Wako Pure Chem. Ind.), SrTiO_3 (Soekawa Rika-gaku), Bi_2O_3 (Wako Pure Chem. Ind.) and MoS_2 (Wako Pure Chem. Ind.) were also commercially available. The surface area of some of the catalyst materials employed in this study is TiO_2 (P-25) 52 m^2 / g ; TiO_2 (T-805) 37 m^2 / g ; TiO_2 (rutile) 16 m^2 / g ; ZnO 3.8 m^2 / g ; and MoS_2 1.1 m^2 / g, which were measured with a Yuasa Ionics Monosorp specific surface area equipment. Water used throughout was doubly deionized and distilled.

**Photolysis procedures**

Each surfactant aqueous solution (0.1 mM, 50 mL) was placed with a catalyst (100 mg) in a 72-mL pyrex bottle and sonicated for 5 min. The sealed suspension in the bottle was saturated with oxygen gas. The above suspended solution was then irradiated with a Toshiba SHLS-1002A mercury lamp (100 W) under magnetic stirring. A 3-mL aliquot was sampled and analyzed by the disappearance of the appropriate UV absorption peak belonging to the surfactant being examined after the removal of catalyst particles by filtration and/or centrifugation (the decomposition of the aromatic ring was examined at 224 nm for DBS and BS, and at 220 nm for BDDAC and BTAC). The oxygen consumption and the CO_2 evolution were monitored by gas chromatography using a Molecular sieve column and a Porapack Q column, respectively. The SO_4^{2-} ion was assayed by ion chromatography through a Shodex I-524 A anionic column using an aqueous phthalic acid solution (10 mM) as an eluent solution.

**Results and discussion**

The photocatalytic degradation of DBS by various semiconductor catalysts is shown in Fig. – 1. The ring cleavage rate of DBS by
ZnO was the most rapid among the semiconductor catalysts used. Even surface-modified TiO₂ (T-805) catalyst, which is commonly employed in cosmetics, also caused the photooxidation. The rutile TiO₂ and MoS₂ could scarcely degrade DBS. Catalysts of WO₃ and ZrO₂ also exhibited low photocatalytic activities. The rutile TiO₂ particulates, prepared by calcination above 600°C, exhibited low photocatalytic activities. By contrast, the anatase TiO₂ particulates prepared by calcination below 600°C showed excellent photocatalytic activities. The reason for this difference in activity has not been clarified until now. One possible causes may be that formation of -OH and -OOH radicals is depressed at the surface of the rutile catalyst. As the content of Pt metal loaded on TiO₂ powders increased, the photocatalytic degradation was lowered. Interestingly, a lower platinum content as in TiO₂/Pt (0.73 %) or TiO₂/Pt (1.0 %) made this material more photocatalytic than TiO₂/Pt (1.5 %).

Fig.-2 shows the O₂ consumption over anatase TiO₂ in the photodegradation of DBS and dodecylpyridinium chloride (C₁₂-PC). The Pt-loaded TiO₂ catalyst exhibited a lower activity than the naked TiO₂ particles, possibly because electron-transfer from the conduction band of TiO₂ to the O₂ molecule is suppressed owing to prevalent electron transfer to the Pt metallic islands. Oxygen consumption must control the photodegradation of organic substances in the illuminated TiO₂ system. The photoreduction, in which conduction band electrons are trapped by O₂ molecules, is an important rate-determining step. Subsequently, such reactive O₂⁻ radicals are formed that also react with the organic compounds degraded. Consumption of O₂ is slight under dark conditions and in a TiO₂-free system. Control experiments showed that no photooxidative degradation occurs in the absence of TiO₂ and that no thermal degradation takes place in the dark solutions containing the suspended photocatalyst.

The photodegradation of BS without an alkyl chain exhibited the same tendencies as those of DBS with an alkyl chain as shown in Fig.-3. The photodegradation rate varied in the order:

ZnO > TiO₂ (anatase) > TiO₂ (T-805)

No photocatalytic degradation was observed when WO₃, rutile TiO₂ and MoS₂ were used.

Fig.-4 depicts the photodecomposition of BTDAC. Anatase TiO₂ (P-25) exhibited the highest photocatalytic activity for a cationic surfactant. The photooxidation of cationic BTDAC surfactant was slower than that of anionic DBS surfactant with the same catalysts. The absorbance at 220 nm increased initially during the first 30 min of irradiation, since the photooxidized intermediate

![Fig.-2 Oxygen consumption for the photooxidation of DBS and C₁₂-PC(0.1 mM, 50 mL) in the presence of TiO₂ (P-25) and TiO₂ /Pt (1.5 %) particles (100 mg).](image1)

![Fig.-3 Effect of various catalysts (100 mg) (anatase TiO₂, rutile TiO₂, ZnO, WO₃, MoS₂ and ZrO₂) for the photodegradation of BS (0.1 mM, 50 mL).](image2)
(hydroxylated BTDAC) formed also has a band in this region. The photolysis by WO$_3$ and MoS$_2$ catalysts was poor. Although the photocatalytic data of SrTiO$_3$, Bi$_2$O$_3$, and ZrO$_2$ are not illustrated in Fig. 4, BTDAC was scarcely decomposed by these materials.

The photodegradation of BTAC by the various photocatalytic materials is shown in Fig. 5. The cationic BTAC having no long alkyl chain was only slightly decomposed. The order of degradation was as follows:


The formation of SO$_4^{2-}$ ions in the photomineralization of DBS and BS is depicted in Fig. 6. The rate of formation of SO$_4^{2-}$ ions is very fast initially within 20 min. It implies that the photodecomposition is initiated from the sulfuryl moiety of DBS or BS. The ZnO catalyst exhibited higher activity than anatase TiO$_2$. BS was more rapidly decomposed than DBS surfactant in the initial illumination period.

The CO$_2$ evolution from the photomineralization of DBS is shown in Fig. 7. Anatase TiO$_2$ (P-25) evolved CO$_2$ gas in a higher yield. ZnO gave a yield of 80% after 5 h-illumination time. Reaction of ZnO with CO$_3^{2-}$ ions is not excluded. The Pt-loaded TiO$_2$...
catalyst gave only a small quantity of CO₂. The WO₃ exhibited the same tendency as TiO₂/Pt, while the rutile TiO₂ hardly evolved any CO₂ gas.

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References

界面活性剤の光分解（第16報）
界面活性剤の光酸化に関する
種々の半導体の光触媒効果

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TiO₂（アナターゼ型、ルチル型、表面修飾型、白金
塩和型）、ZnO、WO₃などの半導体による陰イオン性
DBS および陽イオン性 BDDAC 界面活性剤の光分
解の触媒効果を調べた。アナターゼ型 TiO₂がルチル型
TiO₂より光触媒能は強い。白金塩和 TiO₂触媒は O₂の
O₂⁻へへの電子供与（光還元）の抑制のため、アナターゼ
型 TiO₂より活性は低く、ZnOは DBS の光酸化に対
して触媒活性が最も高く、他の半導体触媒 WO₃と MoS
は触媒活性が低い。 （連絡者：日高久夫）

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