Retarded Decomposition of the Trimethylammonium Moiety Observed on Photocatalytic Mineralization of Surfactants over TiO_2 Photocatalyst

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The CO_2 evolution rate for photocatalytic mineralization of alkyltrimethylammonium chloride sharply decreased when the mineralization yield became nearly equal to the proportion of the long alkyl carbon to the total organic carbon, suggesting that the photodecomposition rate of the alkyl chains is much faster than that of the trimethylammonium group. Moreover, the presence of Br^- significantly suppressed the initial CO_2 evolution rate, and resulted in incompleted mineralization with the final mineralization yield virtually equal to the proportion of the carbon atoms not attaching to the quarternary nitrogen.

Rapidly emerging environmental problems related to our daily life have triggered an extensive interest in photocatalytic decomposition of organic pollutants over TiO_2 photocatalysts. Many kinds of organic surfactants widely employed for household and industrial purposes are one of the major causes of water pollution. Although some surfantant molecules can be degraded via biological pathways, biolysis of surfactants generally takes a long period of time.[1] Moreover, nonionic surfactants are unsuitable for biolysis because they form insoluble toxic intermediates.[2] Biological decomposition of cationic surfactants has been also reported to be difficult owing to their antibacterial and bactericidal properties.[3] TiO_2 semiconductors exhibit a strong oxidizing power of photogenerated charge carriers, and easily decompose organic species. The TiO_2 photocatalyst is therefore very attractive for elimination of various surfactants as water pollutants. Most of the studies were focused on the photodecomposition behavior depending on the adsorption properties of different surfactants under low surfactant concentrations, while the reports investigating difference in reactivity between carbon atoms within a single surfactant molecule have been scarce in the literature. In this study, we have revealed that the photocatalytic decomposition behavior of alkyltrimethylammonium surfactants strongly reflects their asymmetrical molecular structures and depends on their counterions.

The photocatalytic decomposition of a wide variety of surfactants was carried out in a closed circulating reactor. The following surfactants were used as substrates: sodium dodecylsulfate (C_{12}SO-Na), sodium dodecylphosphate (C_{12}PO-Na), and sodium benzenesulfonate (BzSO-Na) were employed as anionic surfactants, while alkyltrimethylammonium chloride and bromide with different alkyl chain lengths, C_nTMA-Cl/Br (n=8, 12, 16) were cationic. 0.25 g of TiO_2 (Nippon Aerosil, P-25) was suspended into 100 ml of a 0.5 mM aqueous solution of a surfactant in a quartz cell, and was irradiated with a 500 W xenon lamp with continuous magnetic stirring under atmospheric air at room temperature. The amount of CO_2 evolved in the gas phase was determined by gas chromatography directly connected to the reactor. The amount of CO_2 dissolved in the liquid phase was compensated by the solubility of CO_2 in water.

The reaction time courses of the mineralization yield to CO_2 for three anionic surfactants, BzSO-Na, C_{12}SO-Na, and C_{12}PO-Na, are illustrated in Figure 1. The mineralization yields linearly increased with time, and reached straight ca. 100 %. The time required for complete mineralization and the rate of the CO_2 evolution were virtually the same for C_{12}SO-Na and C_{12}PO-Na, those which have the same C_{12} chains but completely different hydrophilic groups. The time of complete mineralization for BzSO-Na containing 6 carbon atoms was nearly equal to the half of that for C_{12}SO-Na or C_{12}PO-Na with 12 carbon atoms. Under our experimental conditions, no difference in the reactivity was observed between the benzene ring and the alkyl chain, and the decomposition rate per carbon atom was practically the same for these three surfactants. The photodecomposition of cationic surfactants also showed little difference in their initial CO_2 evolution rates. Moreover, no dependence on the ionic moieties of the surfactants was observed, even between the anionic and cationic surfactants. Hidaka et al. reported that decomposition of surfactants by TiO_2 photocatalyst could be explained by the Langmuir-Hinshelwood model.[4] Although the decomposition rate of the surfactants depends on their molecular structure at low surfactant concentrations, the light-driven generation of ·OH radicals becomes the rate limiting step as the surfactant concentration increases.[5] Since the surfactant concentration in our experiments is considered to be much excess to the TiO_2 surfaces available for the reactants, the initial photocatalytic activity is presumably independent on the adsorption properties of the surfactants on the TiO_2 surfaces.

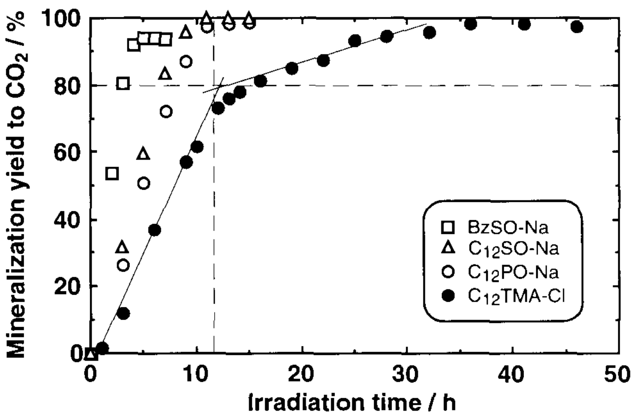

Figure 1. The reaction time courses of the mineralization yield to CO_2 in the photocatalytic decomposition of BzSO-Na, C_{12}SO-Na, C_{12}PO-Na, and C_{12}TMA-Cl by TiO_2.

Although CO_2 linearly evolves until the mineralization completes for most of the surfactants as shown in Figure 1, the CO_2 evolution rate for C_{12}TMA-Cl sharply changed on the way to the completion. The time course of mineralization yield for C_{12}TMA-Cl also shown in Figure 1 indicates that the initial CO_2 evolution rate for C_{12}TMA-Cl was almost the same as that for C_{12}PO-Na having the same dodecyl chain. However, the CO_2 evolution rate suddenly decreased to less than 0.12 times of the initial value, when the mineralization yield reached around 80 %. The mineralization yield of 80 % corresponds to the ratio of the carbon atoms in the dodecyl chain to the total carbon of the C_{12}TMA-Cl molecule. Moreover, the time when the CO_2 evolution rate changed was almost the same as the complete mineralization time of C_{12}PO-Na for which the dodecyl chain contains all of the carbon atoms in the molecule. Although the photodecomposition reaction of the dodecyl chain and the trimethylammonium group is supposed to be a competitive reaction, these results suggest that the dodecyl group in C_{12}TMA-Cl is photodecomposed much faster than the trimethylammonium group. This was further confirmed by the photocatalytic decomposition of C_nTMA-Cl (n=8, 12, 16) shown in Figure 2. The time courses of CO_2 evolution are clearly divided into two steps with the different CO_2 evolution rates also for C_8TMA-Cl and C_{16}TMA-Cl. The amounts of CO_2 evolved when the rate changed were ca. 400 μmol for C_8TMA-Cl and ca. 800 μmol for C_{16}TMA-Cl, matching to the amounts of the carbon atoms contained in their alkyl chains. Moreover, the CO_2 evolution rates observed in the latter step are lower than that of the initial step, and identical for all three surfactants. It is hence probable that the CO_2 evolution in the latter step is attributed to the photodecomposition of carbon atoms with the same reactivity among the three surfactants. These results further suggest that the photodecomposition rate of the alkyl chains would be much faster than that of the trimethylammonium groups, and that in the latter step, the photodecomposition of the trimethylammonium groups having low reactivity would be predominantly observed.

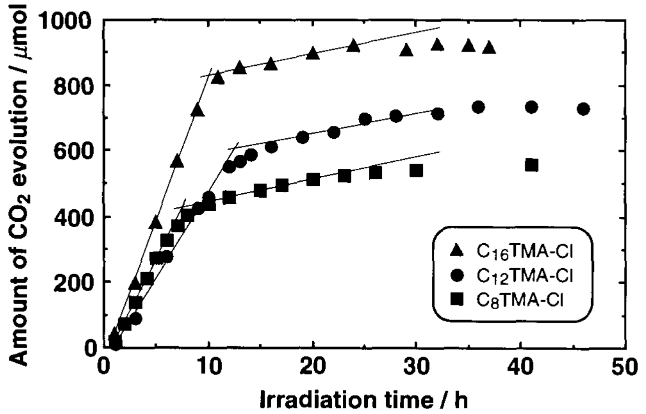

Figure 2. The reaction time courses of the CO_2 evolution in the photocatalytic decomposition of C_8TMA-Cl, C_{12}TMA-Cl, and C_{16}TMA-Cl by TiO_2.

We have also found that the halide counterions strongly influence the decomposition rate of $CnTMA^+$. As shown in Figure 3, the CO_2 evolution from C_{12}TMA-Br was gradually slowed down, and finally ceased before the complete mineralization. The final mineralization yield was ca. 75 %, corresponding well to the ratio of carbon atoms which are not in the vicinity of the quarternary nitrogen atom in the $C_{12}TMA^+$ ion. Similar results were also obtained for C_8TMA-Br and C_{16}TMA-Br. Moreover, the identical behavior in which the CO_2 evolution ceased at mineralization yield of ca. 75% was observed also for C_{12}TMA-Cl when the equivalent amount of KBr coexisted. These results imply that Br^- somewhat deactivates the TiO_2 photocatalyst, and completely hinders the mineralization of the carbon atoms directly bound to the quarternary nitrogen.

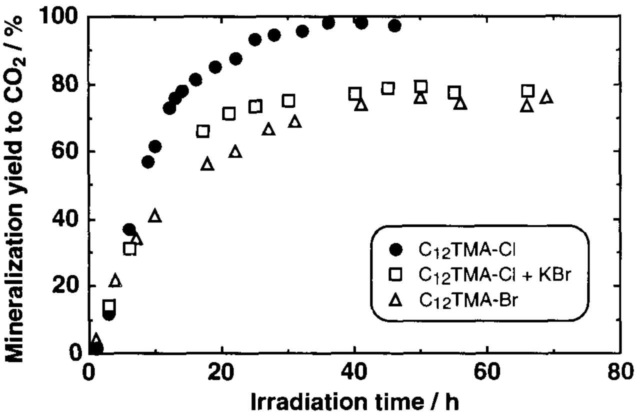

Figure 3. Effects of counterions on the mineralization yield to CO_2 in the photocatalytic decomposition of $C_{12}TMA^+$.

Although the reactivity of surfactant molecules containing nitrogen atom has been reported as pyridine ring > secondary amine > tertiary amine > peptide bond > quarternary amine,[6] there has been no observation of the different reactivity within a single surfactant molecule. The two-step behavior observed in our experiment is, therefore, very interesting. Moreover, investigation for influence of coexisting ions on the photocatalytic activity would be very important in terms of practical use, since the deactivation by Br^- might be observed also for various kinds of surfactants and different photocatalytic reactions. In order to elucidate the mechanism of the two steps-behavior and deactivation of TiO_2 photocatalyst by Br^- observed on the decomposition of alkyltrimethylammonium surfactants, the detailed studies, for example, the detection of intermediates in the reaction mixtures, are in progress.

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