FULL PAPER

Decomposition of 2-naphthol in water by TiO_2 modified with SnO_x or $(\text{Mn}, \text{Sn})\text{O}_x$ and MnO_x Daichi TANAKA¹, Toshihiro ISOBE¹, Sachiko MATSUSHITA¹ and Akira NAKAJIMA^{1,†}¹Department of Materials Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Titanium dioxide (TiO_2) surface was modified with MnO_x , SnO_x or $(\text{Mn}_{0.8}, \text{Sn}_{0.2})\text{O}_x$ by chemisorption calcination cycle (CCC) processing. Samples modified with SnO_x or $(\text{Mn}_{0.8}, \text{Sn}_{0.2})\text{O}_x$ were also modified with MnO_x by subsequent CCC processing. Then the decomposition activity on 2-naphthol in water was evaluated at 50°C in the dark or under visible light illumination. The modification with MnO_x engendered a decrease in the sample bandgap. Although the samples modified with SnO_x or $(\text{Mn}_{0.8}, \text{Sn}_{0.2})\text{O}_x$ only did not show decomposition activity in the dark, they decomposed 2-naphthol in water by subsequent modification with MnO_x on their surface. The results suggest that the interaction between the base material and modified MnO_x plays an important role on the activity order. Samples modified with SnO_x or $(\text{Mn}_{0.8}, \text{Sn}_{0.2})\text{O}_x$ and MnO_x exhibited decomposition activity both in the dark and under visible light. Although the activity in the dark decreased gradually through repeated use, it recovered by ultraviolet light illumination at room temperature or heating at 300°C in ambient air.

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1. Introduction

Titanium dioxide (TiO_2) is a well-known semiconductor photocatalyst. When ultraviolet light (UV) light is illuminated on this material, electron and hole pairs are generated.¹⁾ The electron and hole pairs respectively reduce and oxidize adsorbates on the surface, thereby producing radical species such as $\cdot\text{OH}$, O_2^- , $\cdot\text{HO}_2$, and H_2O_2 , which can decompose most organic compounds and bacteria. Numerous studies of this material have been conducted for its applications to environment purification.^{2)–6)}

Because of its bandgap (3.2 eV for anatase, 3.0 eV for rutile), photocatalytic reaction by pure TiO_2 requires illumination with light of a wavelength that is sufficiently short for electron excitation, which is in the UV range and which constitutes only a small fraction of the full sunlight spectrum. Combining materials with decomposition activity against organic substances in the dark with TiO_2 enables continuous environmental purification throughout the day.

Recent investigations have revealed that manganese-based oxides (MnO_x) decompose organic compounds without light illumination under ordinary pressure at temperatures less than 100°C.^{7)–11)} Their decomposition activity (oxidation) is attributed to the Mars–van Krevelen (MvK) mechanism.^{8),10),11)} Very recently, we modified a

TiO_2 surface with MnO_x by chemisorption calcination cycle (CCC) processing.¹²⁾ The decomposition activities of the materials on 2-naphthol were evaluated in water at 50°C with and without visible light illumination. Both the decomposition activity in the dark and the visible light photocatalytic activity were induced in TiO_2 by modification with MnO_x . The results show that the activity in the dark resulted from the MvK mechanism. Synergistic effects on decomposition in the dark were inferred for the combination of MnO_x and CeO_y . Decomposition activity in the dark decreased via repeated use, but it recovered by UV illumination and subsequent heat treatment in ambient air.

In the MvK mechanism, oxidation of organic compounds proceeds by reduction of MnO_x . The reduced MnO_x is expected to be oxidized again by oxygen (or dissolved oxygen). Actually, Mn(IV) can be reduced through Mn(III) to Mn(II). Therefore, the high concentration ratio of Mn(IV) in MnO_x implies a large amount of oxidation capability with respect to organic compounds. Zhang et al. impregnated various carbon materials with MnO_2 and investigated the reduction temperature of MnO_2 using H_2 -TPR.¹³⁾ They demonstrated that the reduction temperatures for both $\text{Mn(IV)} \rightarrow \text{Mn(III)}$ and $\text{Mn(III)} \rightarrow \text{Mn(II)}$ depend on the base material impregnated with MnO_2 . The decomposition activity of MnO_x when deposited onto TiO_2 might also be affected by the base materials. Both α - MnO_2 and SnO_2 possess rutile-type crystal structures with different lattice constants.¹⁴⁾ Given this background, we modified

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TiO₂ (rutile-type) surface with MnO_x, SnO_x or (Mn_{0.8}, Sn_{0.2})O_x through CCC processing for the present study. We can expect (Mn_{0.8}, Sn_{0.2})O_x to occupy an intermediate state between MnO_x and SnO_x. The samples modified with SnO_x or (Mn_{0.8}, Sn_{0.2})O_x were also modified with MnO_x by subsequent CCC processing. Then the activity of the powders on the decomposition of 2-naphthol in water was investigated with and without light illumination, because earlier studies had evaluated decomposition activity of the materials prepared by CCC processing on 2-naphthol in water.^{8),12),21)} In the present study, we specifically emphasized examination of the activity in the dark.

2. Experimental

2.1 Sample preparation and characterization

All starting chemicals used in this study were reagent-grade. A commercial rutile-type TiO₂ powder (MT150A; Tayca Corp., Osaka, Japan) was fired at 600°C for 1 h in air. It was then impregnated with precursors of MnO_x, SnO_x or (Mn_{0.8}, Sn_{0.2})O_x by CCC process. The TiO₂ powder (1.2 g) was dispersed into ethanol solutions (8.0 mmol/L, 12 mL) of manganese(III) acetylacetonate [Mn(acac)₃; Wako Pure Chemical Industries Ltd., Tokyo, Japan], tin(IV) bis(acetylacetonate) dichloride [Sn(acac)₂Cl₂; Sigma-Aldrich Corp., U.S.A.] or a mixture of these solutions [molar ratio: Mn(acac)₃/Sn(acac)₂Cl₂ = 4/1] and was stored for 24 h. After filtration and washing, the powder was dried under a vacuum for 24 h. Then it was fired at 500°C for 1 h in air. This impregnation–calcination cycle was repeated three times for MnO_x modification and two times for SnO_x or (Mn_{0.8}, Sn_{0.2})O_x modification. The resulting samples are designated respectively as Mn3, Sn2 and (MnSn)2 in this study. The number included in the name signifies the repetitions for modification. Subsequently, some Sn2 and (MnSn)2 were modified with MnO_x using the same procedure for three cycles. These samples are designated as Sn2–Mn3 and (MnSn)2–Mn3 in this study. A schematic illustration of the surface modification is presented in **Fig. 1**.

The crystalline phase of the powder was evaluated using X-ray diffraction (XRD, XRD-6100; Shimadzu Corp., Tokyo, Japan). Specific surface areas were measured using the Brunauer–Emmett–Teller (BET) method with N₂ (BEL SORP mini; Bel Japan Inc., Tokyo, Japan). Morphological features of the powder were observed using a scanning electron microscope (SEM, JEM-7500F; JEOL Ltd., Tokyo, Japan). The ultraviolet–visible light (UV–Vis)

absorption spectra were obtained using a UV–Vis scanning spectrophotometer (V-660; Jasco Corp., Tokyo, Japan). Then the bandgap value was obtained by drawing lines tangent to the Kubelka–Munk function plots of the obtained spectra assuming the allowed indirect transition. The surface chemical composition was measured using an X-ray photoelectron spectroscopy (XPS, ESCA 5500MT; PerkinElmer Inc., U.S.A.) with an AlK α X-ray line (1486.6 eV). The valences of Mn were ascertained through deconvolution of the Mn2p peak, as in earlier studies.^{15)–19)} Moreover, the obtained powder was soaked in distilled water (2.0 g/L) for 6 h. The dissolved ion concentration in water was evaluated using inductively coupled plasma analysis (Prodigy ICP; Leeman Labs, Hudson, NH., U.S.A.)

2.2 Decomposition activity measurement

A solution of 2-naphthol (C₁₀H₇OH; Wako) was prepared by dissolution into an acetonitrile (C₂H₃N; Wako)–water mixture (1:99 volume ratio) solvent (2-naphthol concentration: 4.0×10^{-5} mol/L). The modified TiO₂ powder was dispersed into the solution heated at 50°C (by 0.2 g/100 mL). The suspension was stirred at 270 rpm with air bubbling at 120 mL/min. After filtration, the 2-naphthol concentration in the solution was analyzed from absorption at 223 nm, which is characteristic of 2-naphthol,²⁰⁾ using UV–Vis spectra. To evaluate the temperature dependence, similar activity evaluation was also conducted for (MnSn)2–Mn3 at 60 and 70°C.

Illumination experiments were conducted in a square Pyrex glass vessel (5 cm $\times$ 5 cm $\times$ 8 cm) under the same conditions using a light-emitting diode (LPWI-1007II; Hayashi Watch Works, Tokyo, Japan) with a Y-44 filter (Asahi Glass Co. Ltd., Japan). Because of this experimental setup, the contribution of light within the wavelength range that is feasible for pure rutile excitation was almost negligible. Light illumination was conducted continuously. Its intensity at the inner front surface of the vessel was 6.87×10^3 lux.

Moreover, the effect of UV illumination or heat treatment on the decomposition activity after repeated reaction in the dark was evaluated using (MnSn)2–Mn3. The decomposition activity on 2-naphthol in water at 50°C was evaluated in the dark following the procedure described above. The sample was filtrated and dried at room temperature in vacuum for 24 h. Then the decomposition activity measurement in the dark was conducted again. After drying at room temperature, UV illumination (light intensity: 1.5 mW/m² at 380 nm by black-light bulb) for 72 h or heat treatment at 300°C for 4 h in ambient air was conducted. After these treatments, the activity measurements were conducted again in the dark.

3. Results and discussion

3.1 Character of obtained samples

XRD revealed that all the obtained powders were rutile single phase (**Fig. 2**). **Figure 3** presents SEM micrographs

Fig. 1. Schematic illustration of surface modification.

of the obtained powders. The rutile particle size was 20–100 nm, but the images showed no remarkable morphological change occurring during modification. The specific surface area of the TiO₂ powder before modification was 35 m²/g. That of other modified powders was within 10% of this value (32–34 m²/g). The powder color, which changed from white to light brown with modification by MnO_x, is thought to have originated from Mn(III) and Mn(IV). The dissolution concentration of Mn and Sn into distilled water during stirring for 6 h was negligible: on the order of parts per billion.

Table 1 presents surface chemical compositions obtained from XPS analysis. The chemical composition values in the table were the atomic ratios obtained by assuming Ti as 100. The differences in Mn amounts between Sn2–Mn3 and Sn2, and between (MnSn)2–Mn3 and (MnSn)2 were, respectively, 13.2 and 12.8. These values are almost equivalent to the Mn amount in Mn3 (13.2). This result implies that the Mn amounts transferred onto TiO₂, Sn2 and (MnSn)2 by three-cycle-modification using the MnO_x precursor solution are almost identical. The amount ratio between Mn and Sn in (MnSn)2 was

Fig. 2. XRD patterns of prepared samples.

Fig. 3. SEM micrographs of prepared samples: (a) TiO₂; (b) Mn3; (c) Sn2–Mn3; and (d) (Mn,Sn)2–Mn3.

5.3/1.1(Mn/Sn), which was nearly the same molar ratio as that of the starting composition. However, we were unable to observe the portions or clusters of these chemical species on the powder surface even using a transmission electron microscope (TEM). Similar results were also reported from earlier studies,^{8),12)} suggesting that the cluster size resulting from CCC processing is quite small or thin.

Table 2 presents the valence of Mn obtained from XPS. The valence of Sn was IV for all Sn-containing samples. The amounts of MnO₂ were 43–50% for Mn3, Sn2–Mn3 and (MnSn)2–Mn3. No significant difference was found among the samples. This might be due to the sharing of the same type (rutile) of crystal structure among α -MnO₂, TiO₂ and SnO₂. The UV–Vis spectra of TiO₂, Mn3, Sn2–Mn3 and (MnSn)2–Mn3 are depicted in **Fig. 4**. The band-gap values obtained by converting UV–Vis spectra to Kubelka–Munk function plots are presented in **Table 3**. The modification of MnO_x engendered a decrease in the bandgap of the samples. We confirmed that the valence band (VB) top decreases (becomes negative) concomitantly with increases in the MnO_x amount.¹²⁾ This trend was confirmed for TiO₂ modified with transition metal oxide clusters by the CCC process, suggesting the forma-

Table 1. Chemical compositions of samples obtained from XPS analysis

Sample name	Ti	Mn	Sn
TiO ₂	100	—	—
Mn3	100	13.2	—
(MnSn)2	100	5.3	1.1
(MnSn)2–Mn3	100	18.1	0.6
Sn2	100	—	5.9
Sn2–Mn3	100	13.2	6.0

Table 2. Valence states of Mn in the samples

Sample name	MnO	Mn ₃ O ₄	MnO ₂
Mn3	0	56.8	43.2
Sn2–Mn3	0	49.9	50.1
(MnSn)2–Mn3	0	54	46

Fig. 4. UV–Vis spectra of TiO₂, Mn3, Sn2–Mn3, and (MnSn)2–Mn3.

Table 3. Bandgaps of the samples

Sample name	E _g (eV)
TiO ₂	2.98
Mn ₃	2.65
Sn ₂	2.99
Sn ₂ -Mn ₃	2.76
(MnSn) ₂	2.91
(MnSn) ₂ -Mn ₃	2.44

Fig. 5. Concentration changes of 2-naphthol in water at 50°C in the dark. **Fig. 6.** Temperature dependence of the concentration changes of 2-naphthol in water for (a) (MnSn)₂-Mn₃ in the dark and (b) its Arrhenius plots.

tion of a Ti-O-Mn interfacial bond yielding a surface d sub-band, which disperses around the energy level to overlap with the VB of TiO₂, as proposed by Tada and Jin.^{8),21)} The decrease in the bandgap can be attributed to formation of the d sub-band.

3.2 Decomposition activity in the dark and under visible light

Figure 5 presents the concentration changes of 2-naphthol in water at 50°C in the dark. Pure TiO₂, Sn₂ and (MnSn)₂ exhibited almost no concentration change during 6 h, except during the initial 1 h. However, decreased concentration of 2-naphthol after 1 h was observed clearly for Mn₃, Sn₂-Mn₃, and (Mn,Sn)₂-Mn₃. **Figure 6(a)** depicts the temperature dependence of the concentration changes of 2-naphthol in water for (MnSn)₂-Mn₃ in the dark. Among all the samples, this sample exhibited the greatest concentration decrease in the dark. The rate of the concentration decrease of 2-naphthol accelerated with increases in temperature. This decrease in

concentration cannot be explained merely by adsorption, suggesting the involvement of decomposition. Both decomposition and adsorption contribute to the concentration change in the early stage of the reaction in this system. Therefore, we used concentration results from 1 to 6 h for the calculation of reaction constant for the decomposition activity in accordance with the previous study.¹²⁾ The apparent activation energy obtained from an Arrhenius plot [Fig. 6(b)] of the results in Fig. 6(a) was 27.7 kJ/mol. This value is within the range of reported values (22.2–48.9 kJ/mol) for the oxidation of organic compounds by MnO_x.^{12),22),23)} This result suggests that the decomposition of 2-naphthol in water at 50°C in the dark proceeds by the MvK mechanism. The activation energy for the diffusion of organic substances in water is, at most, 20 kJ/mol.²⁴⁾ Therefore, this reaction might be governed not by substance transport but rather by the surface reaction.

The results presented in Fig. 5 imply that the decomposition activity of Sn₂-Mn₃ and (Mn,Sn)₂-Mn₃ was induced by MnO_x modified through secondary modification. The order and practical values of the reaction constants for Mn₃, Sn₂-Mn₃ and (Mn,Sn)₂-Mn₃ are Sn₂-Mn₃ ($2.0 \times 10^{-2}/\text{h}$) < Mn₃ ($2.8 \times 10^{-2}/\text{h}$) < (Mn,Sn)₂-Mn₃ ($3.7 \times 10^{-2}/\text{h}$). The results of XPS analysis revealed that the concentration and valence state of MnO_x are almost equivalent for Mn₃, Sn₂-Mn₃, and (Mn,Sn)₂-Mn₃. A plausible explanation for the reaction constant order for these three samples was the difference in the base materials of the modified MnO_x. As described above, α-MnO₂, SnO₂ and TiO₂ possess the same (rutile-type) crystal structure. Their lattice constant order for them is SnO₂ ($a = 0.4737 \text{ nm}$, $c = 0.3185 \text{ nm}$) > TiO₂ ($a = 0.4593 \text{ nm}$, $c = 0.2959 \text{ nm}$) > MnO₂ ($a = 0.4395 \text{ nm}$, $c = 0.2860 \text{ nm}$).¹⁴⁾ Several epitaxial relations were reported among these materials.^{26)–28)} Therefore, the formation of a certain amount of SnO₂ and (Mn_{0.8}Sn_{0.2})O₂ can be expected on the surface of Sn₂ and (MnSn)₂. Assuming MnO₂ formation on these surfaces, the lattice mismatch order considering Vegard's law is expected to be Sn₂-Mn₃ > Mn₃ > (MnSn)₂-Mn₃, which is the inverse trend of the reaction constant. Differences in the base materials might also affect the concentration ratio of polymorphs of MnO₂ such as the β-phase or γ-phase. As reported by Zhang et al,¹³⁾ the base materials might contribute to the stability of MnO_x and to the resultant decomposition activity by the MvK mechanism.

Because of a smaller redox potential than that of Mn, and the requirement of multiple electron reaction for the reduction (Sn⁴⁺/Sn²⁺: 0.154 V vs. SHE @25°C, MnO₂/Mn₂O₃: 0.98 V vs. SHE @25°C²⁵⁾), tin should not exhibit a significant contribution to the decomposition by the MvK mechanism under the present experimental condition. Perhaps for that reason, Sn₂ and (MnSn)₂ exhibited poor decomposition activity in the dark. In the case of (MnSn)₂, it can be inferred that solid-solution formation inhibits the reduction of Mn to decompose 2-naphthol.

Figure 7 shows the effects of visible light illumination for samples with decomposition activity in the dark [Mn₃,

Fig. 7. Effects of visible light illumination on the concentration decrease of 2-naphthol in water at 50°C for Mn3, Sn2-Mn3, and (Mn,Sn)2-Mn3.

Sn2-Mn3 and (Mn,Sn)2-Mn3] on the concentration decrease rate of 2-naphthol in water at 50°C. The reaction constant order was Mn3 ($2.8 \times 10^{-2}/\text{h}$) < (MnSn)2-Mn3 ($6.4 \times 10^{-2}/\text{h}$) < Sn2-Mn3 ($8.2 \times 10^{-2}/\text{h}$). The effects of visible light illumination were evident for Sn2-Mn3 and (Mn,Sn)2-Mn3, although they were not significant for Mn3 despite the decreasing bandgap. However, a sample with high Mn concentration (Mn/Ti = 23/100) exhibited clear visible light photocatalytic activity, suggesting that insufficient photon absorption is a main reason for the Mn3's slight difference between in the dark and under visible light. Because of sufficient photon absorption caused by a small bandgap, (MnSn)2-Mn3 exhibited visible light photocatalytic activity. Although the bandgap was greater than Mn3 (see Table 2), Sn2-Mn3 exhibited the highest photocatalytic activity of the three under visible light. Jin et al. modified rutile surface by SnO_x using CCC processing and demonstrated that the modification increases photocatalytic activity. They have conducted density functional theory calculations and have attributed the activity improvement to the increased density of states near the CB minimum of rutile by hybridization with the SnO₂ cluster levels through interfacial Ti–O–Sn bonds, which enables an increase in light absorption and enhancement of charge separation.²⁹⁾ Several powder characteristics of Sn2 such as slight band-narrowing, the valence state of Sn, and invisible clusters under TEM, correspond to their study. For this reason, a similar mechanism can also be expected to be present on the Sn2-Mn3 surface. It can be inferred that Sn2-Mn3 exhibited the highest visible light photocatalytic activity because of the combination of the effect of SnO_x with that of MnO_x. This study demonstrated that (MnSn)2-Mn3 and Sn2-Mn3 possess decomposition activity of 2-naphthol in water at 50°C, both in the dark and under visible light.

Figure 8 depicts the reaction constants for (MnSn)2-Mn3 with repeated use and subsequent UV illumination or heat treatment. Repeated use decreased the decomposition activity of (MnSn)2-Mn3. A similar trend was reported for Mn3 in our previous study, and was attributed to the slow re-oxidation rate of the reduced MnO_x by dissolved

Fig. 8. Reaction constants for (MnSn)2-Mn3 in the concentration change of 2-naphthol in water at 50°C in the dark with repeated use, and after UV illumination or heat treatment at 300°C.

oxygen during the MvK mechanism in water.¹²⁾ When UV light was illuminated onto the samples in the dark after (MnSn)2-Mn3 was used twice, the decomposition activity recovered. That recovery became remarkable when heat treatment at 300°C was applied. These results demonstrated that decreased decomposition activity in the dark caused by repeated use is recoverable by use of these treatments, and suggest that the re-oxidation of reduced MnO_x proceeded efficiently by photocatalytic reaction or high-temperature oxidation. Because MnO_x contacted TiO₂ directly, the activity recovery is believed to occur smoothly with UV illumination. The decomposition activity after heat treatment at 300°C exceeded the initial values. This result was attributable to oxidation beyond that of the initial state.¹²⁾

4. Summary

In this study, MnO_x, SnO_x or (Mn_{0.8}, Sn_{0.2})O_x was used to modify TiO₂ surface by CCC processing. The samples modified with SnO_x or (Mn_{0.8}, Sn_{0.2})O_x were also modified with MnO_x by subsequent CCC processing. The decomposition activities of the materials on 2-naphthol were evaluated in water at 50°C with and without visible light illumination. XPS analysis revealed that the amounts of MnO_x contributing decomposition activity in the dark are almost equal for Mn3, Sn2-Mn3, and (MnSn)2-Mn3. The activity order in the dark suggested a contribution of base materials to the stability of MnO_x. Both Sn2-Mn3 and (MnSn)2-Mn3 exhibited decomposition activities for 2-naphthol in water at 50°C in the dark and under visible light. Decomposition activity in the dark decreased with repeated use, but it recovered with UV illumination or heating at 300°C in ambient air.

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