

Decomposition of 2-Naphthol in Water by Brookite-Type TiO₂ Modified with MnO_x and CeO_y Under Dark Condition

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Abstract

Brookite-type TiO₂ was modified with MnO_x and CeO_y by chemisorption calcination cycle (CCC) process. Then the decomposition activity on 2-naphthol in water was evaluated for these samples at 50°C in the dark. The decomposition activity increased concomitantly with the increase of the MnO_x modification cycle. Subsequent modification of CeO_y onto a MnO_x-modified sample slightly increased the decomposition activity. The modification of CeO_y raised the decomposition rate remarkably when the modification order between MnO_x and CeO_y was converted, suggesting the importance of interaction between the base material and modified MnO_x.

Key-words: Mn, Ce, Brookite, 2-naphthol, Dark

1. Introduction

Numerous studies have been conducted of titanium dioxide (TiO₂), a well-known semiconductor photocatalyst¹, for its application to environmental purification²⁻⁶. Although TiO₂ is safe and abundant in nature, one shortcoming is the requirement of UV light, only a small fraction of the entire sunlight spectrum, for electron excitation. Combining materials with decomposition activity against organic substances in the dark with TiO₂ enables continuous environment purification throughout the day.

Recent investigations have revealed that MnO_x decomposes organic compounds in the dark under normal pressure at temperatures less than 100°C⁷⁻¹¹. Their activity is attributed to the Mars-van Krevelen (MvK) mechanism^{8,10,11}. Very recently, we modified MnO_x onto a rutile-type TiO₂ surface by chemisorption calcination cycle (CCC) processing¹². The decomposition activity of the materials on 2-naphthol was evaluated in water at 50°C. Both the decomposition activity in the dark and the visible light photocatalytic activity were provided to TiO₂ by modification of MnO_x. The results revealed that the dark activity originated from the MvK mechanism. Synergistic effects on decomposition in the dark were inferred for the subsequent loading of CeO_y after MnO_x modification. In the MvK mechanism, oxidation of organic compounds proceeds with reduction of MnO_x. The reduced MnO_x is expected to be oxidized again by oxygen (or dissolved oxygen). An earlier study revealed that CeO₂ works as oxygen reservoir to oxidize MnO_x¹³.

Actually, reductions of Mn (Mn(IV)→Mn(III)→Mn(II)) and Ce (Ce(IV)→Ce(III)) via repeated use were confirmed for this material system¹². Therefore, decomposition in the dark gradually decreased via repeated use, but recovered as a result of heat treatment in ambient air.

In our earlier study, effects of MnO_x and CeO_y modification on dark activity are less remarkable for anatase than for rutile¹². One plausible explanation is the interaction between base material and MnO_x. Zhang *et al.* demonstrated that the reduction temperatures for both Mn(IV)→Mn(III) and Mn(III)→Mn(II) depend on the base material impregnated with MnO₂¹⁴. α -MnO₂ possesses a rutile-type crystal structure¹⁵. Therefore, activation energy for reduction of MnO_x might be different between anatase and rutile. Three TiO₂ polymorphs are rutile, anatase, and brookite. Although anatase has been used widely as a photocatalytic material, several reports have described the high photocatalytic activity of brookite^{16,17}. For the present study, using the CCC process, we modified brookite-type TiO₂ particles with MnO_x and CeO_y. Then, the activity of the powders on the decomposition of 2-naphthol in water was investigated in the dark, as in earlier studies^{8,12}.

2. Experimental

2.1 Sample preparation and characterization

All starting chemicals used for this study were reagent-grade. A brookite-type TiO₂ powder (Titanium(IV) Oxide, 99.99%, Koujundo Chemical Lab. Co. Ltd.) was fired at 500°C for 1 h in air. The TiO₂ powder (1.2 g) was