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

Yirong Qi*, Mimori Shiohara*, Daichi Tanaka*, Toshihiro Isobe*, Sachiko Matsushita* and Akira Nakajima*.†

* Department 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
† Corresponding Author, E-mail: anakajim@ceram.titech.ac.jp

(Received November 13, 2017; Accepted January 9, 2018)

Abstract
Brookite-type TiO₂ was modified with MnOₓ and CeOₙ 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 MnOₓ modification cycle. Subsequent modification of CeOₙ onto a MnOₓ-modified sample slightly increased the decomposition activity. The modification of CeOₙ raised the decomposition rate remarkably when the modification order between MnOₓ and CeOₙ was converted, suggesting the importance of interaction between the base material and modified MnOₓ.

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

1. Introduction
Numerous studies have been conducted of titanium dioxide (TiO₂), a well-known semiconductor photocatalyst[1], for its application to environmental purification[2-6]. 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 MnOₓ decomposes organic compounds in the dark under normal pressure at temperatures less than 100°C[7-11]. Their activity is attributed to the Mars-van Krevelen (MvK) mechanism[8,10,11]. Very recently, we modified MnOₓ onto a rutile-type TiO₂ surface by chemisorption calcination cycle (CCC) processing[12]. 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 MnOₓ. 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 CeOₙ after MnOₓ modification. In the MvK mechanism, oxidation of organic compounds proceeds with reduction of MnOₓ. The reduced MnOₓ is expected to be oxidized again by oxygen (or dissolved oxygen). An earlier study revealed that CeO₂ works as oxygen reservoir to oxidize MnOₓ[13].

Actually, reductions of Mn (Mn(IV)→Mn(III)→Mn(II)) and Ce (Ce(IV)→Ce(III)) via repeated use were confirmed for this material system[12]. 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 MnOₓ and CeOₙ modification on dark activity are less remarkable for anatase than for rutile[12]. One plausible explanation is the interaction between base material and MnOₓ. 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 MnO₂[14]. α-MnO₂ possesses a rutile-type crystal structure[15]. Therefore, activation energy for reduction of MnOₓ 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 MnOₓ and CeOₙ. 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