

## Decomposition of 2-Naphthol in Water by Brookite-Type TiO<sub>2</sub> Modified with MnO<sub>x</sub> and CeO<sub>y</sub> Under Dark Condition

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### Abstract

Brookite-type TiO<sub>2</sub> was modified with MnO<sub>x</sub> and CeO<sub>y</sub> 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<sub>x</sub> modification cycle. Subsequent modification of CeO<sub>y</sub> onto a MnO<sub>x</sub>-modified sample slightly increased the decomposition activity. The modification of CeO<sub>y</sub> raised the decomposition rate remarkably when the modification order between MnO<sub>x</sub> and CeO<sub>y</sub> was converted, suggesting the importance of interaction between the base material and modified MnO<sub>x</sub>.

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

### 1. Introduction

Numerous studies have been conducted of titanium dioxide (TiO<sub>2</sub>), a well-known semiconductor photocatalyst<sup>1</sup>, for its application to environmental purification<sup>2-6</sup>. Although TiO<sub>2</sub> 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 TiO<sub>2</sub> enables continuous environment purification throughout the day.

Recent investigations have revealed that MnO<sub>x</sub> decomposes organic compounds in the dark under normal pressure at temperatures less than 100°C<sup>7-11</sup>. Their activity is attributed to the Mars-van Krevelen (MvK) mechanism<sup>8,10,11</sup>. Very recently, we modified MnO<sub>x</sub> onto a rutile-type TiO<sub>2</sub> surface by chemisorption calcination cycle (CCC) processing<sup>12</sup>. 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 TiO<sub>2</sub> by modification of MnO<sub>x</sub>. 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<sub>y</sub> after MnO<sub>x</sub> modification. In the MvK mechanism, oxidation of organic compounds proceeds with reduction of MnO<sub>x</sub>. The reduced MnO<sub>x</sub> is expected to be oxidized again by oxygen (or dissolved oxygen). An earlier study revealed that CeO<sub>2</sub> works as oxygen reservoir to oxidize MnO<sub>x</sub><sup>13</sup>.

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<sup>12</sup>. 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<sub>x</sub> and CeO<sub>y</sub> modification on dark activity are less remarkable for anatase than for rutile<sup>12</sup>. One plausible explanation is the interaction between base material and MnO<sub>x</sub>. 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 MnO<sub>2</sub><sup>14</sup>.  $\alpha$ -MnO<sub>2</sub> possesses a rutile-type crystal structure<sup>15</sup>. Therefore, activation energy for reduction of MnO<sub>x</sub> might be different between anatase and rutile. Three TiO<sub>2</sub> 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<sup>16,17</sup>. For the present study, using the CCC process, we modified brookite-type TiO<sub>2</sub> particles with MnO<sub>x</sub> and CeO<sub>y</sub>. Then, the activity of the powders on the decomposition of 2-naphthol in water was investigated in the dark, as in earlier studies<sup>8,12</sup>.

### 2. Experimental

#### 2.1 Sample preparation and characterization

All starting chemicals used for this study were reagent-grade. A brookite-type TiO<sub>2</sub> powder (Titanium(IV) Oxide, 99.99%, Koujundo Chemical Lab. Co. Ltd.) was fired at 500°C for 1 h in air. The TiO<sub>2</sub> powder (1.2 g) was