**Communications**

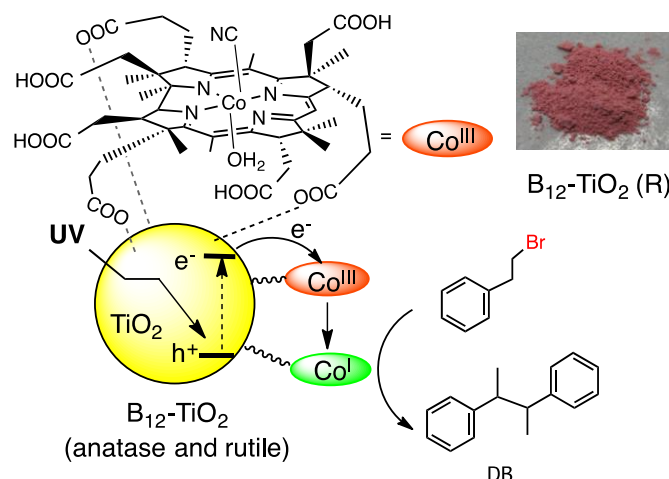# Crystal Structure Dependence for Reactivities of B$_{12}$-TiO$_2$ Hybrid Catalysts with Anatase and Rutile Forms

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**ABSTRACT**: The debromination of phenethyl bromide by the B$_{12}$-TiO$_2$ hybrid catalyst under UV light irradiation was investigated. The catalytic efficiency was dependent on the type of TiO$_2$. The anatase form of TiO$_2$ was superior to the rutile form of TiO$_2$. The selectivity of the product was also dependent on the crystal structure of TiO$_2$, and the rutile form of TiO$_2$ showed a high selectivity for the formation of the coupling product, 2,3-diphenylbutane, when compared to that of the anatase form of TiO$_2$.

The application of titanium oxide (TiO$_2$) has increased in various areas such as organic synthesis, solar cell devices, antibiotic and environmental applications, and surface selfcleaning due to its semiconductor property.[1-4] We recently reported the preparation and catalysis of TiO$_2$ combined with a cobalamin derivative (B$_{12}$), cyanoaqua cobyrinic acid, [(CN)(H$_2$O)Cob(III)7COOH]Cl.[5-10] Naturally-occurring B$_{12}$(cobalamin)-dependent enzymes catalyze various molecular transformations that are of particular interest from the viewpoint of biological chemistry as well as synthetic organic chemistry and catalytic chemistry.[11-17] The B$_{12}$- TiO$_2$ hybrid catalyst also shows a unique catalysis for the dechlorination of organic halides,[5-7] radical-mediated organic synthesis,[8,9] alkene reduction and hydrogen evolution.[10] It is well-known that TiO$_2$ particles generate electron-hole pairs under band gap excitation by UV light irradiation and the conductive band electron (e$_{CB}^-$) for TiO$_2$ has an $E_{red}$ of –0.5 V and –0.3 V *vs*. NHE (in pH 7 aqueous solution) in the anatase and rutile, respectively.[1] In contrast, the redox potentials for the Co$^{III}$/Co$^{II}$ and Co$^{II}$/Co$^{I}$ couples of cobalamin derivatives are observed at around +0.2 and –0.3 *vs*. NHE in various media.[18] Therefore, it was possible to generate the reactive Co$^{I}$ species of B$_{12}$ via electron transfer from TiO$_2$ by UV light irradiation, and we succeeded in performing various B$_{12}$ dependent reactions mediated by the supernucleophilic Co$^{I}$ form of B$_{12}$. In previous studies, we mainly used P-25 TiO$_2$ (Japan Aerosil) which is a mixture of the anatase (80%) and rutile (20%) forms.[5] We have now investigated a comparison of the anatase- and rutile- structured TiO$_2$ during the catalysis of the B$_{12}$-TiO$_2$ hybrid catalyst as shown in **Figure 1**. We found a crystal structure dependency for the catalysis of B$_{12}$-TiO$_2$ regarding the reaction efficiency and selectivity.

The B$_{12}$-TiO$_2$ hybrid catalyst was prepared by a previously reported method.[5] The content of the B$_{12}$ complex on the surface of the anatase (A) TiO$_2$ (AMT-600, average surface area: 52 m$^2$/g, TAYCA Co., Ltd.) was 1.75x10$^{-5}$ mol/g and the apparent surface coverage by the B$_{12}$ complex was 3.4x10$^{-11}$ mol/cm$^2$, while the B$_{12}$ complex content on the surface of the rutile TiO$_2$ (R) (TK-1005, average surface area: 52 m$^2$/g, TAYCA Co., Ltd.) was 2.13x10$^{-5}$ mol/g and the apparent surface coverage by the B$_{12}$ complex was 4.1x10$^{-11}$ mol/cm$^2$.

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**Figure 1.** Structure of B$_{12}$-TiO$_2$ hybrid catalyst. Photograph is of the rutile form of TiO$_2$ immobilized with the cobalamin derivative, cyanoaqua cobyrinic acid, [(CN)(H$_2$O)Cob(III)7COOH]$^+$.

We initially examined the reductive formation of the Co$^{I}$ species of B$_{12}$ on the surface of TiO$_2$ under UV light irradiation by diffuse reflectance (DR) UV-vis spectroscopy. Both B$_{12}$-TiO$_2$ hybrids (atanase and rutile forms) suspended in MeOH showed the typical DR UV-vis spectra for the Co$^{I}$ state of B$_{12}$ with a reflectance maxima at 390 nm and 570 nm after UV light irradiation as shown in **Figures 2a** and **2b**, respectively. The Co$^{II}$ complex having absorption maximum at 470 nm were transitionally formed during UV light irradiation as shown in **Figure 2**. The time for the Co$^{I}$ formation was different in the anatase- and rutile- TiO$_2$s. To complete the reaction, the anatase-type TiO$_2$ requires 50 seconds, while the rutile-type TiO$_2$ required 300 seconds. Therefore, the anatase TiO$_2$ was superior to the rutile TiO$_2$ for the formation of the Co$^{I}$ species since the conduction band electron is more negative in the anatase TiO$_2$ ($E_{red}$ = -0.5 V vs. NHE in pH 7 aqueous solution) than that of the rutile ($E_{red}$ = -0.3 V vs. NHE in pH 7 aqueous solution). This is an advantage for the B$_{12}$ catalytic reaction, which is mediated by the reactive Co$^{I}$ species.

To confirm the difference in TiO$_2$ using the catalysis of B$_{12}$- TiO$_2$, we carried out a catalytic reaction using two types of TiO$_2$s. For the catalytic reaction, 500 equivalent moles of phenethyl bromide (3.0x10$^{-3}$ M) versus the B$_{12}$ complex on the TiO$_2$ were dissolved in MeOH, and nitrogen gas was bubbled to remove the oxygen, then irradiated using black light (365 nm). After the photoreaction, the products were identified by GC-MS. The results are summarized in **Table 1**. 2,3-Diphenylbutane (mixture of racemi and meso) (DB) and ethylbenzene (EB) were obtained as products. Of course, the reaction did not proceed in the absence of B$_{12}$ using bare TiO$_2$ (entries 5 and 6 in **Table 1**).
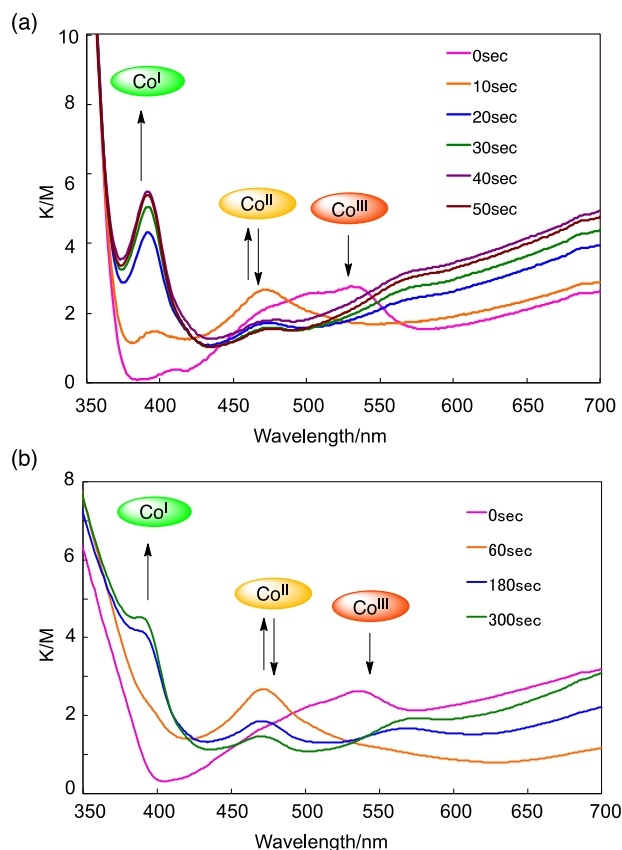
**Figure 2.** Diffuse reflectance (DR) UV-vis spectral change in $B_{12}$-$TiO_2$ during UV light irradiation in MeOH under $N_2$. (a) Using anatase $TiO_2$, and (b) rutile $TiO_2$.

Conversions of the substrate were 44 % (entry 1 in **Table 1**) and 57 % (entry 2 in **Table 1**) for $B_{12}$-$TiO_2$ (R) and $B_{12}$-$TiO_2$ (A), respectively. The high conversion of $B_{12}$- $TiO_2$(A) is probably due to the efficient formation of the reactive $Co^I$ species by the anatase $TiO_2$. This behavior was consistent with the DR UV-vis change in **Figure 2**. The selectivity of the coupling product (DB) over the simply reduced product (EB) was 67 % and 38 % for $B_{12}$-$TiO_2$(R) and $B_{12}$-$TiO_2$ (A), respectively.[19] When the $B_{12}$ complex was not immobilized on $TiO_2$, but dissolved in the solution in which heptamethyl cobyrinate perchlorate[20] was used as the $B_{12}$ complex, the coupling product (DB) was scarcely formed (entries 3 and 4 in **Table 1**). After the photoreaction, some amount of $B_{12}$ was desorbed on the surface of $B_{12}$ and the desorption of $B_{12}$ was 33 % in $B_{12}$-$TiO_2$ (R) (entry 1 in **Table 1**) and 68 % in $B_{12}$- $TiO_2$ (A) (entry 2 in **Table 1**). In other words, the $B_{12}$ was more stably immobilized on the surface of the rutile $TiO_2$. Based on these results, we proposed the reaction mechanism as shown in **Figure 3**. The coupling product DB could be formed by $B_{12}$ on the $TiO_2$, while EB was formed by $B_{12}$ desorbed from $TiO_2$. The coordination modes of the carboxylates on the anatase- and rutile- $TiO_2$ phases were revealed by confocal Raman microscopy.[21] Such distinct coordination modes could affect the stability of the $B_{12}$ complex immobilized by carboxylates anchor on the $TiO_2$ surface. The selective formation of DB in $B_{12}$-$TiO_2$ (R) (entry 1 in **Table 1**) may be caused by stability of $B_{12}$ complex on $TiO_2$. Substrate radical derived from alkylated complex on $TiO_2$ (R) should be formed in close distance, which is favorable for coupling reaction to form DB. And it should be noted that difference of photocatalytic activity between anatase and rutile $TiO_2$ is dependent on many factors not only band potential of $TiO_2$ but also crystallinity, particle size, surface morphology and so on.[22-24] The difference for catalysis of $B_{12}$ complex combined with anatase and rutile forms of

$TiO_2$ also might be affected by other factors. Further study on $B_{12}$-$TiO_2$ catalysis is in progress in our laboratory.
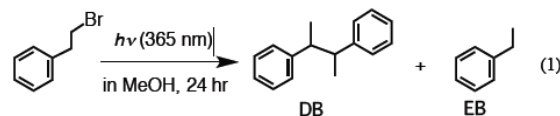


**Table 1.** Reduction of phenethyl bromide catalyzed by $B_{12}$-$TiO_2$ under $N_2$ at room temperature in MeOH[a]

| Entry | Catalyst | Conversion[b] / % | Products (Yield[c] /%) | | Selectivity[c] / % | Desorption of $B_{12}$ / % |
|---|---|---|---|---|---|---|
| | | | DB | EB | | |
| | | | rasemi | meso | | |
| 1 | $B_{12}$-$TiO_2$(R)[d] | 44 | 12 | 12 | 12 | 67 | 33 |
| 2 | $B_{12}$-$TiO_2$(A)d | 57 | 8 | 8 | 26 | 38 | 68 |
| 3 | $B_{12}$, $TiO_2$(R)[e] | 10 | 0 | 0 | 11 | 0 | |
| 4 | $B_{12}$, $TiO_2$(A)[e] | 28 | 1 | 1 | 24 | 7 | |
| 5 | $TiO_2$ (R)[f] | trace | - | - | trace | - | - |
| 6 | $TiO_2$ (A)[f] | trace | - | - | trace | - | - |

[a] Condition: [substrate]=3.0 x$10^{-3}$ M (1.0x$10^{-4}$ mol), catalyst ($B_{12}$-$TiO_2$)=8.5 mg (R) and 10.3 mg (A) (each $B_{12}$, 6.0x$10^{-6}$ M), in 30 mL $CH_3OH$ under $N_2$ at room temperature; reaction time=24 h.
[b] Conversions were estimated by the recovery of the substrate. Yields were based on initial concentration of the substrate.
[c] Selectivity was calculated by {yield of DB/(yield of DB+yield of EB)}x100.
[d] Immobilization amount of $B_{12}$=2.13x$10^{-5}$ mol/g for $TiO_2$(R), 1.75x$10^{-5}$ mol/g for $TiO_2$ (A). [e]Condition: [substrate]=3.0 x$10^{-3}$ M, $TiO_2$ (10 mg), cyanoaqua heptamethyl cobyrinate, 0.22 mg (6.0x$10^{-6}$ M), solvent 30 mL $CH_3OH$ under $N_2$ at room temperature, reaction time=10 h. [f] Unmodified 10 mg of $TiO_2$ was used.
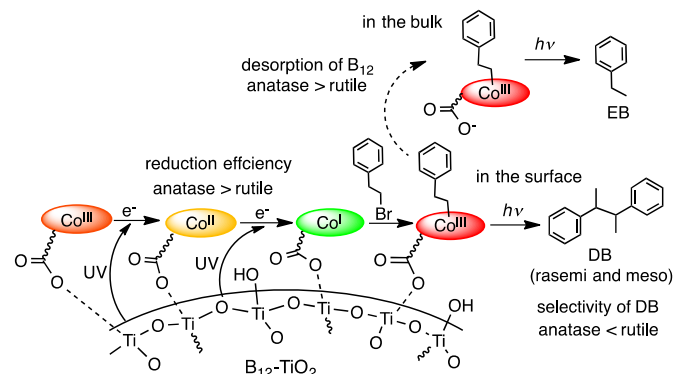


**Figure 3.** Plausible mechanism for selective formation of 2,3-diphenylbutane catalyzed by $B_{12}$-$TiO_2$.

In conclusion, we have developed the $B_{12}$-$TiO_2$ hybrid catalyst for a light-induced catalytic reaction. The reaction efficiency was dependent on the reducing ability of $TiO_2$ caused by the conduction band level. The product selectivity was dependent on the stability of the $B_{12}$-$TiO_2$ composite. This crystal form dependence for the catalysis of $TiO_2$ is useful information for the design of hybrid catalysts. Research is in progress on further preparations of the $TiO_2$ hybrid catalyst with various metal complexes in our laboratory.

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