B_{12}–TiO_2 Hybrid Catalyst for Dehalogenation of Organic Halides

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A cobalamin derivative, cobyrinic acid, was effectively immobilized on TiO_2, and the hybrid TiO_2 was characterized by UV–vis, XPS, MALDI-TOFMS as well as TEM analysis. The hybrid TiO_2 exhibits high reactivity for dehalogenation of various organic halides such as phenethyl bromide, benzyl bromide, and 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) under irradiation with UV light at room temperature.

Cobalamin-dependent enzymes catalyze various molecular transformations that are of particular interest from the viewpoint of biological chemistry as well as organometallic and catalytic chemistry.[1] One of the most significant properties of cobalamin is the high nucleophilicity toward various alkyl halides in its Co^I state to form an alkylated complex with dehalogenation.[2] As cobalamin derivatives are involved in the enzymatic reduction of chlorinated organic compounds by a variety of anaerobic bacteria,[3] reductive dechlorination of organic halides, ubiquitous pollutants such as polychlorinated alkenes and alkanes, catalyzed by cobalamin derivatives has been reported.[4] Recently, we also reported the dechlorination of an environmental pollutant, 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) utilizing a cobalamin derivative, heptamethyl cobyrinate $[Cob(II)7C_1ester]ClO_4$, as catalyst under electrochemical and photochemical conditions.[5] The recent requirement of green chemistry along with economical and environmental pressures has led chemists to attempt to utilize a more efficient and clean catalyst while using a simpler and more facile system. Therefore, we tried to construct a new cobalamin derivative (B_{12})-dependent dehalogenation system utilizing titanium dioxide (TiO_2) photosensitizer. It is well known that TiO_2 particles generate electron–hole pairs under band gap excitation with UV light irradiation (eq 1).

$$TiO_2 \xrightarrow{h\nu} h_{VB}{}^+ + e_{CB}{}^- \quad (1)$$

The conductive band electron ($e_{CB}{}^-$) for anatase-type TiO_2 has an E_{red} of -0.5 V vs. NHE in pH 7 aqueous solution.[6] In contrast, the redox potential for the Co^{II}/Co^I couple of cobalamin derivatives is observed at -0.3 to -0.4 vs. NHE in various media. Therefore, it is possible to generate the reactive Co^I species of cobalamin derivatives via electron transfer from TiO_2 under irradiation with UV light. Thus in the present paper we describe a novel catalytic system for dehalogenation of various organic halides utilizing cobalamin derivative (B_{12}) immobilized on TiO_2 photosensitizer as shown in Figure 1. Similar hybrid TiO_2 systems have been reported,[7,8] and cobalt phthalocyanine and cobalt porphyrin were used in these papers.

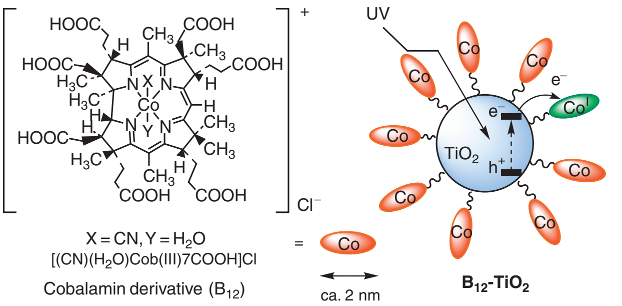

Figure 1. Schematic representation of cobalamin derivative (B_{12})–TiO_2 hybrid catalyst.

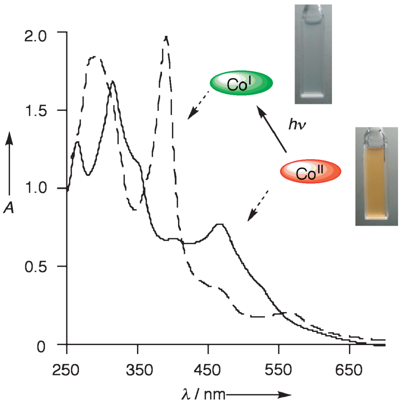

Figure 2. Electronic absorption spectra of $[Cob(II)7C_1ester]ClO_4$ (8.7×10^{-5} M) in ethanol (solid line) containing TiO_2 (P-25, 0.2 mg) and after irradiation with UV light (20 min, broken line).

First, we examined the reductive formation of a Co^I species of a cobalamin derivative by UV–vis spectroscopy in the presence of TiO_2 under irradiation with UV light (365 nm). The cobalamin derivative, $[Cob(II)7C_1ester]ClO_4$, shows typical UV–vis absorption spectrum in ethanol as shown in Figure 2 (solid line). The solution then changed from brown to dark green and showed a typical UV–vis spectrum for the Co^I state of the cobalamin derivative[2b] with absorption maximum at 390 nm after irradiation with UV light as shown in Figure 2 (broken line). As oxidized product, acetaldehyde diethyl acetal was detected by GC-MS. This UV–vis spectral change was not observed in the absence of TiO_2 and suggested that the cobalamin derivative was reduced to a Co^I species by photoinduced electron transfer from TiO_2.

The B_{12}–TiO_2 hybrid catalyst was prepared as follows: TiO_2 powder (P-25; a mixture of rutile (20%) and anatase (80%) with a BET surface area of $50\,m^2\,g^{-1}$, Japan Aerosil) was suspended in ethanol containing 10 mM cobalamin derivative, cyanoaqua cobyrinic acid $[(CN)(H_2O)Cob(III)7COOH]Cl$ (see the Supporting Information[9]) at room temperature. After stirring for 24 h, red-purple TiO_2 was filtered and washed with ethanol, then dried under vacuum. The B_{12}–TiO_2 hybrid catalyst was characterized

Table 1. Dehalogenation of various alkyl halides catalyzed by B_{12}–TiO_2 hybrid catalyst[a]

Entry	Substrate	Conversion[b]/%	Product (Yield[b]/%)
1	$PhCH_2CH_2Br$	95	EB (76), DB (4)
2[c]	$PhCH_2CH_2Br$	trace	trace
3[d]	$PhCH_2CH_2Br$	0	—
4	$PhCH_2Br$	99≈	toluene (2), bibenzyle (94)
5[e]	DDT	99≈	DDD (13), TTDB(E/Z) (30/3), DDA ethyl ester (12), DDMU (16), DDMS (13)
6[e]	DDD	82	DDMU (30), DDMS (35), DCS (15)

[a]Conditions: $[B_{12}–TiO_2] = 20\,mg$, $[substrate] = 3.0 \times 10^{-3}$ M, solvent: 30 mL of EtOH under N_2, reaction time 24 h. [b]Conversions were estimated by the recovery of the substrate. Yields were based on initial concentration of the substrate. [c]Unmodified-TiO_2 (P-25, 19 mg) was used as catalyst. [d]Solvent, 30 mL of CH_3CN. [e]DDD, 1,1-bis(4-chlorophenyl)-2,2-dichloroethane; TTDB, 1,1,4,4-tetrakis(4-chlorophenyl)-2,3-dichloro-2-butene; DDA ethyl ester, ethyl bis(4-chlorophenyl)acetate; DDMU, 1,1-bis(4-chlorophenyl)-2-chloroethylene; DDMS, 1,1-bis(4-chlorophenyl)-2-chloroethane; DCS, 3,6-dichlorophenanthrene (Chart S1).[9]

by high-resolution (HR)-TEM, UV–vis, and MALDI-TOF mass spectrometry as well as XPS analysis. The UV–vis diffusion reflectance analysis showed a reflectance maximum around 520 nm which is characteristic of the α-band of cyanoaqua cobyrinic acid.[1,2b] XPS peaks at 780.4 (Co2p), 458.6 (Ti2p), and 398.8 eV (N1s) were observed. The MALDI-TOF mass spectrum (Figure S2)[9] showed intense peaks at 964, 952, and 938, which are ascribed to $[M^+ - H_2O]$, $[M^+ - CN]$, and $[M^+ - H_2O - CN]$ of $[(CN)(H_2O)Cob(III)7COOH]^+$, respectively. The content of cobyrinic acid immobilized on the surface of TiO_2 was determined by UV–vis analysis to be $3.5 \times 10^{-5}\,mol\,g^{-1}$, and the apparent surface coverage with the cobyrinic acid was $7.0 \times 10^{-11}\,mol\,cm^{-2}$. Modification of the surface of TiO_2 with B_{12} was directly observed by HR-TEM. From the TEM image shown in Figure S1,[9] we can see an amorphous phase with a thickness of ca. 2 nm on TiO_2. The thickness of this amorphous phase is nearly consistent with the size of B_{12}.

Dehalogenation of organic halide was carried out as shown in Table 1. The starting phenethyl bromide almost disappeared, and ethylbenzene (EB) and 2,3-diphenylbutane (mixture of racemi and meso) (DB) were produced in 76% and 4% yields, respectively (Entry 1, Table 1). The turnover number based on the B_{12} catalyst immobilized onto the TiO_2 was over 100. After reaction, the hybrid catalyst was readily recovered by filtration. The dehalogenation reaction did not proceed when we used unmodified-TiO_2 (Entry 2, Table 1) under the same conditions. In acetonitrile, the reaction was completely inhibited (Entry 3, Table 1), since hole ($h_{VB}{}^+$) consumption did not occur and recombination of the electron–hole pair was preferred in contrast with the ethanol solvent system. Indeed, the UV–vis spectral change of a cobalamin derivative shown in Figure 2 did not occur in acetonitrile. These results indicate that formation of Co^I species of B_{12} via electron transfer from TiO_2 is essential for this reaction. Thus formed super-nucleophilic Co^I species reacts with organic halide with dehalogenation. Dehalogenation of various organic halides also efficiently occurred as shown in Table 1.

In conclusion, a B_{12}–TiO_2 hybrid catalyst was readily prepared from cobyrinic acid and TiO_2. The hybrid catalyst showed high reactivity for dehalogenation of various organic halides under irradiation with UV light. We believe that this system would be applicable to the design of new green catalysts for various molecular transformations.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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