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Preparation and Reactivity of Vitamin B_{12}–TiO_2 Hybrid Catalyst Immobilized on a Glass Plate

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The vitamin B_{12}–TiO_2 hybrid catalyst was effectively immobilized on a glass plate, and the immobilized catalyst shows an efficient reactivity for various molecular transformations, such as the 1,2-migration of a phenyl group and dechlorination of perchloroethylene during irradiation by UV light.

Immobilized catalyst is generally considered to hold many advantages, such as utilization of small amounts of catalyst, usable in various media, and ready separation of products and catalyst.[1] The catalyst can be recovered and recycled resulting in reducing waste generated. Cobalt complexes, i.e. vitamin B_{12} derivatives (B_{12}), are good catalysts for several molecular transformations,[2] and efforts toward immobilization of vitamin B_{12} derivatives on various supports have been achieved by several groups.[3] Utilizing the property of B_{12} derivative to react with various organic halides by dehalogenation in the Co(I) state, an efficient dehalogenation system has been constructed.[4] Furthermore, cleavage of the cobalt–carbon bond of the intermediately formed alkylated complex should afford radical species which can be utilized for radical-mediated organic reactions.[5] Recently, we reported the construction of a B_{12} catalytic system utilizing titanium dioxide as a photosensitizer.[6] The UV light irradiation of the hybrid catalyst composed of the B_{12} derivative (cyanoaquacobyrinic acid) and TiO_2 promoted several molecular transformations such as the dechlorination of 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD), the 1,2-migration of a phenyl group, and ring-expansion reactions.[6] In this catalyst, immobilized B_{12} on TiO_2 was reductively activated by band gap excitation of TiO_2 with UV light irradiation. The present study further advanced this B_{12}–TiO_2 hybrid catalytic system from the viewpoint of green chemistry. The previous powdered B_{12}–TiO_2 system requires filtration during the work-up procedure. During filtration, some powdered catalyst was lost and contaminated the product solution. To improve this step, the B_{12}–TiO_2 hybrid catalyst was immobilized on a glass plate as shown in Figure 1 since one of the merits of the TiO_2 particle is that it is easily attached to the surface of various substrates, such as glass.[7]

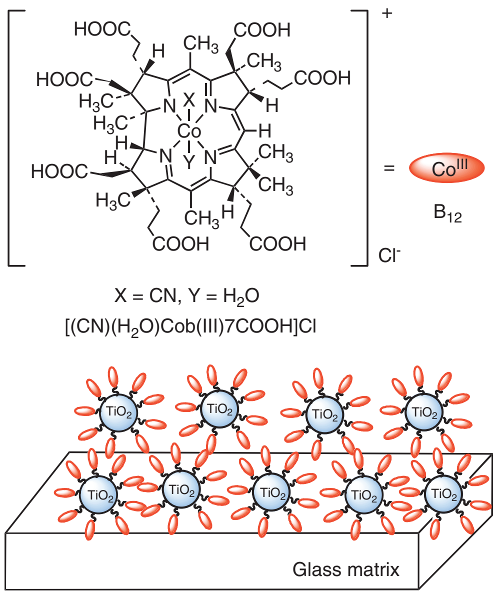

Figure 1. Schematic representation of B_{12}–TiO_2 glass plate.

The B_{12}–TiO_2-coated glass plate was prepared by the following procedure. A TiO_2 sol solution was deposited on a freshly cleaned slide glass substrate by dip coating, and then the glass plate was immersed in a 10 mM aqueous solution of the B_{12} derivative. The glass plate was dried at room temperature. The prepared hybrid glass plate was characterized by UV–vis, XPS, XRD, and SEM. From the UV–vis absorption spectrum, the characteristic absorption maxima of B_{12} were observed at 352, 455, 498, and 529 nm, and the apparent surface coverage of B_{12} was determined to be 2.5×10^{-9} mol cm^{-2}. From the SEM image, growth of a porous film containing B_{12}–TiO_2 nanoparticles was clearly observed as shown in Figure 2. The thickness of the TiO_2 film was ca. 300 nm, which is controlled by changing the rate of the dip-coating. Due to this porous structure, the substrate can access the B_{12} catalytic center within the film.

To confirm this, axial ligation of the cobalt center of B_{12} was monitored by UV–vis. As the hybrid glass plate was immersed in an imidazole methanol solution, the spectrum changed to one with absorption maxima at 359, 465, 518, and 554 nm as shown in Figure 3. This spectrum was identified as the imidazole-coordinated B_{12} complex.[8] Therefore, it is obvious that the substrate molecules could access the B_{12} catalytic center, and all of the immobilized B_{12} is expected to participate in the catalytic reaction.

A catalytic reaction using the B_{12}–TiO_2 glass plate was carried out as shown in Table 1. The diethyl 2-bromomethyl-2-phenylmalonate (**1**) substrate was converted to products, and the phenyl-migrated product **2** was formed along with the formation of the simply reduced product **3** in ethanol as expressed by eq 1. The reaction did not proceed when we used the B_{12}-unmodified TiO_2 or in the dark as shown by Entries 4

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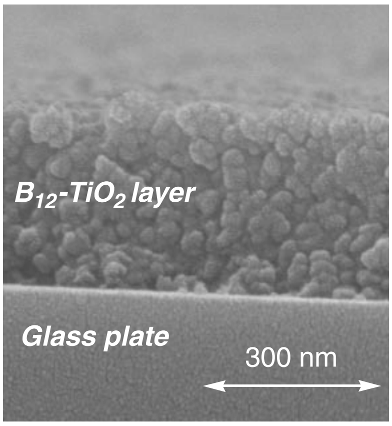


Figure 2. Cross-sectional SEM photograph of the B_{12}–TiO_2 film at a 50 mm min^{-1} withdrawing speed for the dip coating.

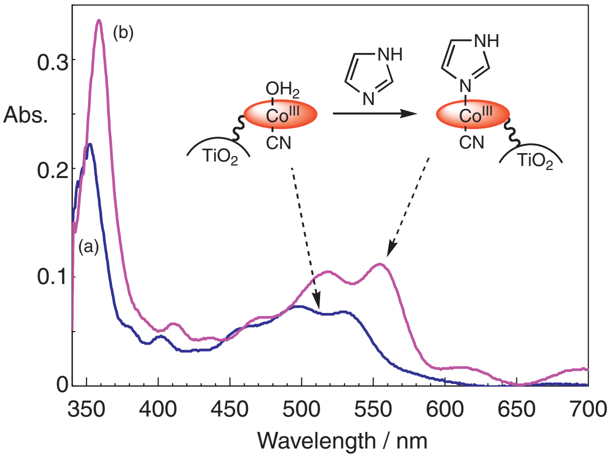
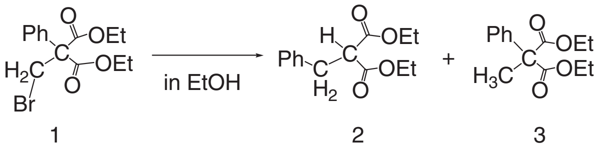


Figure 3. UV–vis spectral change in the B_{12}–TiO_2 glass plate (a) before and (b) after immersion in imidazole solution.

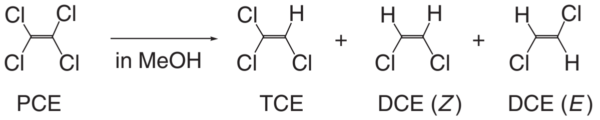


(1)

Table 1. 1,2-Migration of Phenyl Group Catalyzed by B_{12}–TiO_2 System[a)]

Entry	Catalyst	Conversion[b)]/%	Products (Yield[b)]/%)	
			2	**3**
1	B_{12}–TiO_2	59	7	47
2	B_{12}–TiO_2[c)]	56	33	9
3	B_{12}–TiO_2[d)]	trace	—	—
4	TiO_2[e)]	trace	—	—

a) Conditions: [substrate] = 3.0×10^{-3} M (3.0×10^{-5} mol), catalyst (B_{12}–TiO_2 glass): 2.5×5.5 cm^2 (B_{12}, 6.9×10^{-8} mol), solvent: C_2H_5OH (10 mL) under N_2 at room temperature, reaction time: 10 h. b) Conversions were estimated by the recovery of the substrate. Yields were based on the initial concentration of the substrate. c) Solvent, PhCN, triethanolamine (66.7 mg, 4.5×10^{-4} mol, 45 mM) was used as a sacrificial reagent. d) In the dark. e) Unmodified TiO_2 glass plate was used.



(2)

Table 2. Dechlorination of PCE Catalyzed by B_{12}–TiO_2 System[a)]

Entry	Catalyst	Conversion[b)]/%	Products (Yield[b)]/%)	
			TCE	1,2-DCE (*E*/*Z*)
1	B_{12}–TiO_2	59	43	1/1
2	B_{12}–TiO_2[c)]	3	trace	—
3	TiO_2[d)]	trace	—	—

a) Conditions: [PCE] = 1.0×10^{-4} M (1.5×10^{-6} mol), catalyst (B_{12}–TiO_2 glass): 2.5×2.4 cm^2 (B_{12}, 3.0×10^{-8} mol), solvent: CH_3OH (15 mL) under N_2 at room temperature, reaction time: 10 h. b) Conversions were estimated by the recovery of the substrate. Yields were based on the initial concentration of the substrate. c) In the dark. d) B_{12}-unmodified TiO_2 glass plate was used.

and 3 in Table 1, respectively. It was noteworthy that the work-up procedure was significantly simplified in the present system though the conversion decreased to 59% as compared to the powdered system. As for the powdered B_{12}–TiO_2 system, the conversion was 95% under similar conditions.[6b] In the present system, the catalyst immobilized on a glass plate was easily separated from the product. Furthermore, B_{12}–TiO_2 was retained on the glass plate after the reaction, which was confirmed by SEM.

The selectivity of the products was controlled by the solvent.[6b] When the reaction was carried out in a less hydrogen radical donating solvent, the yield of the phenyl-migrated product **2** increased to 33% as shown by Entry 2 in Table 1 since PhCN has a strong C–H bond.[9]

Dehalogenation of an organic chloride was also carried out as shown in Table 2. Perchloroethylene (PCE) was converted to trichloroethylene (TCE) during irradiation by UV light in methanol as expressed by eq 2. As cobalamin derivatives (B_{12}) are involved in the enzymatic reduction of chlorinated organic compounds by anaerobic bacteria,[10] many studies of the dechlorination of PCE were reported using cobalamin derivatives as a catalyst.[11] Among these studies, our system is more convenient and green since the catalyst was activated by simple light irradiation and was easily separated after the reaction.

In conclusion, the heterogeneous B_{12}–TiO_2 hybrid catalyst immobilized on a glass plate was prepared which was inspired from the natural enzyme. The hybrid catalyst showed a high reactivity for molecular transformation under mild conditions. Therefore, the present system would be readily applicable for the design of an eco-friendly catalyst.

Experimental

Apparatus. The NMR spectra were recorded with a Bruker Avance 500 spectrometer at the Center of Advanced Instrumental Analysis of Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual protic solvent peak. The

GC-mass spectra were obtained using a Shimadzu GCMS-QP5050A equipped with a J&W Scientific DB-1 column (length 30 m; ID 0.25 mm, film 0.25 µm). Volatile organic compounds (PCE, TCE, and DCE) were analyzed with a Shimadzu GCMS-QP2010SPG equipped with a Perkin-Elmer Turbo Matrix HS16 using a J&W Scientific DB-624 column (length 60 m; ID 0.32 mm, film 1.80 µm). The UV–vis absorption spectra were measured with a Hitachi U-3300 spectrophotometer at room temperature. Scanning electron micrographs (SEMs) were recorded on a Hitachi S-5000 (HV = 25 kV). The X-ray photoelectron spectroscopy (XPS) experiments were performed with a Physical Electronics XPS 5800. The X-ray diffraction (XRD) analyses were measured with a MacScience Micro-focus X-ray M18XHF diffractometer (Cu Kα, $\lambda = 1.54056$ Å). Dip coatings were performed by an Eintesla MD-408 micro dip-coater.

Chemicals. All solvents and chemicals used in the syntheses were of reagent grade, and were used without further purification. A corrinoid compound (B_{12}), cyanoaquacobyrinic acid ([(CN)-(H_2O)Cob(III)7COOH]Cl), was synthesized using a reported method.[6a] The titanium dioxide sol solution (TS-S4110, anatase) was kindly supplied by Sumitomo Chemical. The diethyl 2-bromomethyl-2-phenylmalonate (**1**) substrate and authentic sample of diethyl 2-methyl-2-phenylmalonate (**3**) were synthesized from diethyl phenylmalonate.[6b] The phenyl-migrated product, diethyl benzylmalonate (**2**), was purchased from Aldrich. Perchloroethylene (PCE) was purchased from GL Science as a methanol solution (5000 µg mL^{-1}).

Preparations of B_{12}–TiO_2 Glass Plate. The TiO_2 sol solution (TS-S4110) was deposited on a freshly cleaned slide glass substrate (Matsunami Glass Industries) by dip coating at withdrawing speeds of 50 mm min^{-1}. The TiO_2 film formed on the substrate was dried for 24 h at room temperature. The obtained glass plate coated with the TiO_2 film was immersed in a 1 mM solution of cyanoaquacobyrinic acid (B_{12}) in H_2O for 30 min. The B_{12} content on the glass plate was determined by UV–vis; B_{12} content: 2.5×10^{-9} mol cm^{-2}. UV–vis λ/nm: 352, 455, 498, 529. XPS E/eV: 780.4 (Co2p), 458.6 (Ti2p), 398.8 eV (N1s). XRD $2\theta/°$: 25.2, 37.8, 48.0, 53.8, 55.0, 62.6 (anatase).

Catalytic Reaction of B_{12}–TiO_2 Glass Plate (General Procedure). The B_{12}–TiO_2 glass plate (area: 2.5×5.5 cm^2 $\times 2$ (both sides), B_{12}: 6.9×10^{-8} mol) was immersed in a 10 mL ethanol solution of a diethyl 2-bromomethyl-2-phenylmalonate (3.0×10^{-5} mol, 3.0 mM) under nitrogen gas atmosphere. The solution was stirred at room temperature under irradiation with 365 nm UV light (1.76 mW cm^{-2} at 12 cm distance). The product was directly analyzed by GC-MS. Diphenyl was used as the internal standard.

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