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Photocatalytic chemoselective cleavage of C–O bonds under hydrogen gas- and acid-free conditions

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In the presence of a palladium-loaded TiO_2 photocatalyst, cleavage of benzyl phenyl ether in low-molecular-weight alcohol solvents under de-aerated conditions afforded toluene and phenol simultaneously in a 1:1 molar ratio.

Reactions that selectively cleave C-heteroatom bonds are important in organic synthesis, in addition to being mechanistically interesting.¹⁻³ Among such reactions, the cleavage of the C-O bonds of biomass constituents has attracted considerable attention. Because almost all chemical products, including plastics, pharmaceuticals, agrochemicals, and cosmetics, are currently produced from fossil resources,⁴ their ongoing depletion means that alternative resources, preferably renewable ones, will need to be developed. Biomass, including lignocellulosic biomass, is a possible alternative source of chemical feedstocks, and methods for the production of aromatic compounds from biomass have been extensively studied. Lignin is the major constituent of lignocellulosic biomass, and the amount of lignin residue produced by the paper industry exceeds 50 million tons/year.⁵ Lignin is also a by-product of the production of ethanol fuel from crop wastes. Lignin is an amorphous polymer comprising aromatic monomers connected via oxygen bridges (C-O bonds), $^{\rm 5,6-8}$ and aromatic compounds can therefore be produced by selective cleavage of the bridges. In addition, lignocellulosic biomass can be obtained from nonfood crops.^{9,10}

Various catalysts have been investigated for the cleavage of lignin C–O bonds to produce aromatic compounds. $^{11-13}\ {\rm For}$

example, noble metal catalysts such as Pt, Pd, and Rh have been used for lignin pyrolysis in the presence of acid and for hydrogenolysis in the presence of H_2 . However, in addition to using expensive catalysts, these reactions require severe reaction conditions (i.e., high temperatures and high H_2 pressures), which result in poor selectivity for the target materials owing to the production of by-products. Therefore, alternative catalytic processes for selective conversion of lignin to aromatic compounds under mild conditions are needed.

One possibility is the use of TiO_2 -mediated photocatalytic redox reactions. Irradiation of TiO_2 with UV light results in the formation of electrons and holes (charge separation), which can then participate in reduction and oxidation reactions, respectively. These redox reactions proceed at room temperature under atmospheric pressure. The use of TiO_2 mediated photocatalysis for organic reactions has been extensively studied.^{14,15} Recently, our research group accomplished photocatalytic reduction (hydrogenation) of nitriles and alkenes by using a TiO_2 -supported catalyst system.^{16,17} We found that strongly reducing hydrogen species were formed photocatalytically. In the current study, photogenerated active hydrogen species were used to accomplish hydrogenolysis of benzyl phenyl ether as a model compound for lignin.

All the chemicals were reagent-grade commercial materials and were used as supplied. Degussa P25, well-known commercial TiO₂ having mixed phase of anatase and rutile, was used as the TiO₂ photocatalyst in this study. Samples of TiO₂ loaded with metal co-catalysts were prepared by a photodeposition method using metal chlorides as precursors, except in the cases of the Rh-, Ag-, and Cu-loaded catalysts, which were prepared with rhodium nitrate (RhNO₃), silver nitrate (AgNO₃), and copper acetate (Cu(CH₃COO)₂), respectively.

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In a typical run, TiO₂ (50 mg) was suspended in 5 cm³ of methanol containing benzyl phenyl ether (50 µmol) in a Pyrex test tube, which was then sealed with a rubber septum under argon and photoirradiated at λ > 300 nm by means of a 400-W high-pressure mercury arc (Sen Lights Corporation, Osaka,

50

40

30

20

10

0

Methanol

Amount /µmol

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adsorption of H_2 .⁴ No reaction occurred in the absence of light or in the absence of a photocatalyst, indicating that the C–O bond was cleaved photocatalytically. To our knowledge, this is the first report of selective cleavage of a C–O bond mediated by a TiO₂ photocatalyst. Although the methanolic Pd-TiO₂ suspension showed much higher activity than the suspensions of the other catalysts, the reaction rate decreased with increasing photoirradiation time, and the reaction stopped almost completely after 120 min (Fig. S2).

Benzyl phenyl ether

Toluene

Phenol



Japan) with magnetic stirring in a water bath maintained at 298 K. The amounts of unconsumed benzyl phenyl ether and

generated toluene and phenol were determined with a gas

chromatograph-mass spectrometry system (GCMS-QP2010

catalysts, we also carried out photocatalytic cleavage reactions

of benzyl phenyl ether at 298 K in methanolic suspensions of

bare TiO₂ or TiO₂ loaded with various metals (Fig. 1) methanol,

Ultra, Shimadzu, Kyoto, Japan) equipped with a HP-1 column. To investigate the effects of nanoparticulate metal co-

Fig. 2 Effects of solvents on photocatalytic cleavage of benzyl phenyl ether over 0.5 wt% Pd-TiO₂ after 30-min photoirradiation.

The material balance calculated by means of Eq. 1 was 100% after 120 min of photoirradiation:

Ethanol

2-Propanol

Solvent

Material balance = $\frac{n(\text{toluene}) + n(\text{phenol}) + 2n(\text{benzyl phenyl ether})}{2n_0(\text{benzyl phenyl ether})}$

(1)

Material balance /%

2-Propanol containing

20 vol% water

where n(toluene), n(phenol), and n(benzyl phenyl ether) are the amounts of toluene, phenol, and benzyl phenyl ether after photoirradiation, respectively, and n_0 (benzyl phenyl ether) is the initial amount of benzyl phenyl ether. This result indicates that no by-products formed and suggests that oxidative such as formaldehyde, deactivated products. the photocatalytic system. The material balance remained at nearly 100% throughout the reaction, indicating that no reaction other than the target reaction occurred and that the reason for the reaction rate decrease was likely to have been poisoning of the catalyst by a product of oxidation of the hole scavenger (i.e., formaldehyde formed by oxidation of methanol by holes). To explore this possibility, we investigated the effects of adding water or aqueous formaldehyde to the reaction mixture (Fig. S3). The addition of 10 vol% water decreased the yields of the cleavage products because the resulting decrease in the methanol concentration negatively affected the rate of electron donation to the valence band of TiO_2 . The reaction rate was decreased even more by the addition of aqueous formaldehyde. These results confirmed that formaldehyde generated by methanol oxidation deactivated the photocatalytic system. We also evaluated the effects of various solvents on photocatalytic cleavage of the C-

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Fig. 1 Effects of metal co-catalysts (0.5 wt%) on photocatalytic cleavage of benzyl phenyl ether in methanolic suspensions under de-aerated conditions after 30-min photoirradiation.

When bare TiO₂ was used as the photocatalyst and the reaction mixture was irradiated for 30 min, no reaction of benzyl phenyl ether occurred, and the TiO₂ turned blue, indicating that Ti⁴⁺ had been reduced to Ti³⁺ bv photogenerated electrons. This result indicates that the holes oxidized the methanol, but the photogenerated electrons in the conduction band of TiO₂ were not involved in cleavage of the benzyl phenyl ether. Nearly identical results were obtained when Cu, Ag, or Au was loaded on the TiO₂ as a co-catalyst. However, when we used Ru-, Rh-, Pd-, or Pt-loaded TiO₂ (denoted as Ru-TiO₂, Rh-TiO₂, Pd-TiO₂, and Pt-TiO₂, respectively), toluene and phenol were obtained in a 1:1 molar ratio by cleavage of the C-O bond of benzyl phenyl ether without the need for H₂ gas. The Pd-TiO₂ catalyst showed much higher yields of toluene and phenol than did the other photocatalysts. All the photocatalysts used in the present reaction show almost same morphology of metal particles as well as similar mean particle size (Fig. S1), indicating that these factors are not crucial for inducing high activity over Pd-TiO₂. Pd-TiO₂ has previously been used for photocatalytic hydrogenation reactions in which an activated hydrogen species (H-Pd) forms by reduction of H⁺.^{16–18} H-Pd also formed in the present system and participated in hydrogenolysis (cleavage) of the C-O bond. It has been reported that Pd catalyst is effective for hydrogenolysis of C-O bond using H₂ gas. Since Pd was also effective in this photocatalytic reaction the active hydrogen species generated system. photocatalytically behave likely that produced by dissociative

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O bond (Fig. 2). When any alcohol was used, no CO₂ was detected. This result indicated that alcohols selectively oxidized to aldehyde or ketone. Photocatalytic reaction of methanol and ethanol over 0.5 wt%Pd-TiO₂ under deaerated condition was performed and no evolution of CO2 was observed for longer photoirradiation (60 min). These results indicated alcohols used in this study could not oxidized to CO₂ in the absence of O_2 . The reaction rate decreased when methanol was replaced with ethanol or 2-propanol (both of which are hole scavengers). Because the addition of water to 2-propanol reportedly has a positive effect on the rate of the photocatalytic dechlorination of chlorobenzene, we also used aqueous 2-propanol containing 20% water for the cleavage reaction.¹⁹ As expected, we obtained the highest reaction rate under these conditions. To investigate the reason why the reaction rate was decreased in ethanol or 2-propanol system, photocatalytic oxidation of alcohols along with H₂ evolution in alcohol suspensions of 0.5 wt% Pt-TiO₂ under deaerated conditions was examined (Fig S4). This reaction system is simple because only alcohols existed in the system and Pt H^{+} is reduced to H₂ selectively, avoiding any other side reactions. Therefore, this photocatalytic H_2 evolution could be used as indicator of the rate of hole trapping. The result of Fig. S4 indicated that reaction rate was decreased by changing methanol to ethanol or 2-propanol because hole-trapping rate was decreased. Although the reaction rate of H₂ evolution from ethanol was faster than 2-propanol, the rate of cleavage of benzyl phenyl ether in ethanol was almost same as 2propanol system. In addition, small amount of benzyl phenyl ether was remained even after 180 min photoirradiation when ethanol was used as solvent. On the other hand, 2-propanol system was completely proceeded. These results indicated that aldehydes formed by oxidation of primary alcohols negatively affected the photocatalytic cleavage of benzyl phenyl ether. Although reaction rate was increased by adding water in 2-propanolic system, water adding negatively affected methanolic system (Fig. 2 and S3). To understand the effect of water on photocatalytic cleavage of benzyl phenyl ether, photocatalytic oxidation of alcohols along with H₂ formation in water-alcohol suspensions of Pt-TiO₂ under deaerated conditions was also examined (Fig S5). This result indicated that water added to 2-propanol affected the two photocatalytic reactions, cleavage of benzyl phenyl ether and H₂ evolution, in a similar way. In addition, we investigated effect of adding water on generation of acetone and H₂ in 2propanolic system (Fig. S6). Although active hydrogen species generated at Pd were used selectively to cleavage of benzyl phenyl ether in water containing 2-propanolic system, H₂ was formed in pure 2-propanol system despite remaining benzyl phenyl ether. These results indicated that adding water affected hole trapping with alcohols and selectivity of reduction though mechanism is not clear.

We evaluated the time courses of the amount of benzyl phenyl ether remaining and the amounts of toluene and phenol generated during photocatalytic cleavage of benzyl phenyl ether in a suspension of 0.5 wt% Pd-TiO₂ in 2-propanol containing 20 vol% water (Fig. 3). The amount of benzyl phenyl

ether started to decrease monotonously immediately after the start of photoirradiation, and toluene and phenol began to form in a 1:1 molar ratio. After 20 min of photoirradiation, the benzyl phenyl ether was almost completely consumed, and high yields of toluene and phenol were obtained (>99% in both cases). After complete consumption of the benzyl phenyl ether, H_2 and acetone began to form (at the same rate), indicating that hydrogenolysis (cleavage) of benzyl phenyl ether competed with H_2 formation and that reduction of benzyl phenyl ether was the dominant reaction. The redox balance was calculated with Eq. (2) and is shown in Fig. 3:

Redox balance = $\frac{2n(\text{converted benzyl phenyl ether}) + 2n(H_2)}{2n(\text{acetone})}$

(2)

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where n(converted benzyl phenyl ether), $n(H_2)$, and n(acetone) are the amounts of consumed benzyl phenyl ether, formed H_2 , and formed acetone, respectively. Throughout the photoirradiation, the redox balance was nearly unity, and no other products were detected upon further photoirradiation, indicating that re-oxidation of the products by holes did not occur and that only 2-propanol was oxidized, accompanied by the production of H₂. It has been reported that in the (thermo)catalytic hydrogenolysis of benzyl phenyl ether over Pd, hydrogenation of phenol and toluene to the corresponding saturated compounds occurs and decreases the yield of toluene and phenol.²⁰ However, because neither high H₂ pressure nor high temperature were used in our system, no hydrogenation occurred, even after the benzyl phenyl ether was completely consumed.

investigated the utility of our photocatalytic We hydrogenolysis protocol by carrying out reactions of various substrates with C-O bonds (Table 1). The protocol was successfully applied to a compound that was bulkier than benzyl phenyl ether (entry 2), as well as to an alkyl ether (entry 3). In addition, even though catalytic hydrogenolysis of the C-O bonds of nitrile compounds with H₂ gas results in reduction of the cyano group to the corresponding amine,²⁰ we found that our photocatalytic system showed high chemoselectivity for the C-O bond. Specifically, when 4-(benzyloxy)benzonitrile was used as the substrate, only the C–O bond reacted with the catalytically generated Pd-H (entry 4). We previously reported that aqueous benzonitrile is photocatalytically hydrogenated without H₂ in the presence of Pd-TiO₂ and oxalic acid as a hole scavenger.¹⁶ The photocatalytic hydrogenation of the cyano group to an amino group was strongly affected by the solvent and hole scavenger.^{13–16} However, the cyano group was not hydrogenated in the 2-propanol system used in this study. Therefore, perfectly chemoselective hydrogenolysis of the C-O bond was achieved. Durability of 0.5 wt% Pd-TiO₂ was investigated with UV-LED (HLV-24UV365, CCS, Kyoto), weaker light intensity than mercury arc, because the rate of reaction was too fast. After the reaction, Pd-TiO₂ was separated from the reaction mixture by simple filtration and reused. The rate of photocatalytic cleavage was decreased with re-used indicating that small amount of 2-propanol or acetone was adsorbed on Pd-TiO₂.

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Irradiation time /min

Fig. 3 Time courses of amounts of benzyl phenyl ether, toluene, phenol, acetone, and H_{2} , along with the redox balance, during photocatalytic cleavage of benzyl phenyl ether in a suspension in 2-propanol containing 20 vol% water and 0.5 wt% Pd-TiO₂.

Table 1 Photocatalytic cleavage of C–O bonds of benzyl ethers in a 2-propanol suspension containing 20 vol% water and 0.5 wt% $\rm Pd\text{-}TiO_2$ after 120-min photoirradiation.

Entry	Compound	Yield of toluene /%	Yield of alcohol /%	Toluene/ Alcohol
1	Benzyl phenyl ether	99	99	1.00
2	Benzyl-2-naphtyl ether	>99	>97	1.02
3	Benzyl butyl ether	>99	99	1.01
4	4-Benzyloxybenzonitrile	>99	>99	1.00

After the reaction (1^{st}) , Pd-TiO₂ was filtered and photoirradiated under O₂ condition, which was used for 2^{nd} reaction (Fig. S7). Tha activity of Pd-TiO₂ was almost same as

 1^{st} reaction, indicating that the adsorptions are easily decomposed to CO₂ by photoirradiation under TiO₂.

In conclusion, in a new example of a TiO₂-photocatalyzed reduction reaction, we examined photocatalytic cleavage of benzyl phenyl ether and found that a Pd co-catalyst had remarkably beneficial effects on the cleavage reaction. The choice of solvent also strongly affected the reaction outcome; specifically, when the reaction was carried out in 2-propanol containing 20 vol% water, no products other than toluene and phenol were obtained. Our results indicate that the utility of H-Pd formed photocatalytically is not limited to hydrogenation reactions and that the protocol described herein constitutes a new strategy for application of photocatalytic reduction of TiO₂.

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Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

- 1 L. A. Goj, M. Lail, K. A. Pittard, K. C. Riley, T. B. Gunnoe and J. L. Petersen, *Chem. Commun.*, 2006, 982.
- 2 A. N. Desnoyer and J. A. Love, *Chem. Soc. Rev.*, 2017, 46, 197.
- 3 K. Sun, Y. Lv, Z. Zhu, L. Zhang, H. Wu, L. Liu, Y. Jiang, B. Xiao and X. Wang, *RSC Adv.*, 2015, **5**, 3094.
- 4 P. S. Rezaei, H. Shafaghat and W. M. A. W. Daud, *Appl. Catal.* A: *Gen.*, 2014, **469**, 490.
- 5 J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552.
- 6 P. Sannigrahi, Y. Pu and A. Ragauskas, *Curr. Opin. Environ. Sustain.*, 2010, **2**, 383.
- 7 J. Lora and W. Glasser, J. Polym. Environ., 2002, 10, 39.
- 8 J. J. Bozell, *Clean Soil, Air, Water,* 2008, **36**, 641.
- 9 A. Demirbaş, Energy Convers. Manage., 2001, 42, 1357.
- 10 M. Stocker, Angew. Chem., Int. Ed. 2008, 47, 9200.
- 11 H. W. Park, J. K. Kim, U. G. Hong, Y. J. Lee, J. H. Song and I. K. Song, *Catal. Surv. Asia*, 2013, **17**, 119.
- 12 M. Kleinert and T. Barth, Energy Fuels, 2008, 22, 1371.
- 13 N. Yan, C. Zhao, P. J. Dyson, C. Wang, L. T. Liu and Y. Kou, *ChemSusChem*, 2008, **1**, 626.
- M.A. Fox and M. T. Dulay, *Chem. Rev.*, 1993, 93, 341.
 G. Palmisano, E. Garcia-Lopez, G. Marci, V. Loddo, S. Yurdakal, V. Augugliaro and L. Palmisano, *Chem. Commun.*, 2010, 46, 7074.
- 16 K. Imamura, T. Yoshikawa, K. Nakanishi, K. Hashimoto and H. Kominami, *Chem. Commun.*, 2013, **49**, 10911.
- 17 K. Imamura, Y. Okubo, T. Ito, A. Tanaka, K. Hashimoto and H. Kominami, RSC Adv., 2014, 4, 19883.
- 18 H. Kominami, M. Higa, T. Nojima, T. Ito, K. Nakanishi, K. Hashimoto and K. Imamura, *ChemCatChem*, 2016, 8, 2019.
- 19 H. Kominami, T. Nishi, K. Fuku and K. Hashimoto, *RSC Adv.*, 2013, **3**, 6058.
- 20 B. Gómez-Monedero, M.P. Ruiz, F. Bimbela and J. Faria, *Appl. Catal. A: Gen.*, 2017, **541**, 60.

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