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Photocatalytic secondary amine synthesis from azobenzenes and alcohols on TiO₂ loaded with Pd nanoparticles[†]

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Photoirradiation ($\lambda > 300$ nm) of TiO₂ loaded with Pd nanoparticles (ca. 2 wt %, 5 nm diameter) in water containing alcohols and azobenzene derivatives at room temperature successfully produces the corresponding secondary amines with high yields. This is facilitated via consecutive photocatalytic and catalytic reactions: (i) photocatalytic oxidation of alcohols (aldehydes formation) and reduction of azobenzenes (anilines formation); (ii) catalytic condensation of the formed aldehydes with anilines on the TiO₂ surface (imines formation); and, (iii) photocatalytic hydrogenation of the formed imines (secondary amines formation). This catalytic system successfully produces several kinds of secondary amines with >80% yields.

Introduction

Azobenzene and its derivatives are very important chemicals in application to dyes, indicators, optical and electronic materials.¹ They have tremendous carcinogenic risks.² Decomposition process of these compounds in industrial wastes is therefore very important for the protection of environment. Several catalytic or photocatalytic decomposition processes have been proposed.³ Recently, as an alternative to the decomposition processes, selective transformation of azobenzenes to valuable chemicals and the reuse of the products for upstream processes have attracted a great deal of attention from the viewpoint of green and sustainable chemistry.⁴ Catalytic hydrogenation of azobenzenes to anilines have mainly been studied.⁵ All of these systems selectively produce anilines, but require expensive reducing agents such as HCO₂NH₂ or relatively high reaction temperatures (>363 K).

Secondary amines are very important intermediates for the synthesis of agricultural chemicals and pharmaceuticals.⁶ They are usually synthesized by N-alkylation of primary amines with alkyl halides; however, this needs excess amount of inorganic bases with a concomitant formation of copious amount of wastes.⁷ An alternative clean way for the secondary amine synthesis is the use of alcohols as alkylating agents with metal catalysts.⁸ These systems promote consecutive catalytic steps in one pot: (a) dehydrogenation of alcohol (aldehyde and H–metal species formation); (b) condensation of the formed aldehyde with amine (imine formation); and, (c) hydrogenation of the imine by the H–metal species (secondary amine formation).

Several heterogeneous catalytic systems have been proposed with PdO_x particles supported on Fe_2O_3 ,⁹ Pd particles supported on boehmite nanofibers,¹⁰ Ag clusters supported on Al_2O_3 ,¹¹ Ru(OH)_x supported on Al_2O_3 ,¹² Au particles supported on TiO_2 ,¹³ and Pd particles supported on MgO.¹⁴ All of these systems selectively produce secondary amines, but require relatively high reaction temperatures (>363 K).



Scheme 1. Proposed mechanism for secondary amine production from alcohol and azobenzene on a Pd/TiO_2 catalyst under UV irradiation.

Herein, we report for the first time a catalytic system that produces secondary amines from alcohols and azobenzenes at room temperature. We use TiO_2 loaded with Pd nanoparticles

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(Pd/TiO₂) as a catalyst under UV irradiation (λ >300 nm). This system promotes consecutive catalytic steps in one pot, as depicted in Scheme 1: (i) photocatalytic oxidation of alcohol (aldehyde formation) and reduction of azobenzene (aniline formation); (ii) catalytic condensation of the formed aldehyde with aniline on the TiO₂ surface (imine formation); and, (iii) photocatalytic hydrogenation of the formed imine (secondary amine formation). The system successfully produces several kinds of secondary amines with very high yields (>80%).

Results and Discussion

Preparation and characterization of catalysts

The Pd_x/TiO_2 catalysts with different Pd loadings [x (wt %) = $Pd/TiO_2 \times 100$; x = 0.5, 1, 2 and 4] were prepared by impregnation of Pd(NO₃)₂ onto P25 TiO₂ (anatase/rutile ratio = $\sim 80/20$; average particle size, 24 nm; BET surface area, 59 m² g⁻¹) followed by reduction with H₂.¹⁵ As shown in Fig. S1 (ESI†), transmission electron microscopy (TEM) images of the catalysts show reveal that all of the catalysts possess spherical Pd particles. As summarized in Table 1, the size of Pd particles increases with the Pd loadings: average diameters for x = 0.5, 1, 2, and 4 catalysts were 2.6, 4.1, 5.0, and 6.5 nm, respectively. As shown in Fig. S2 (ESI†), diffuse-reflectance UV-vis spectra of the catalysts reveal that all of them show characteristic flat absorption at $\lambda > 300$ nm due to the light scattering by the Pd particles.¹⁶

Photocatalytic activity

Efficacy of Pd/TiO₂ catalysts for secondary amine synthesis is confirmed by the reaction of azobenzene and benzyl alcohol. The reaction was performed by photoirradiation ($\lambda > 300$ nm) of water (4.5 mL) containing catalyst (10 mg), azobenzene (12.5 µmol), and benzyl alcohol (0.5 mL) under N₂ atmosphere at 303 K. Table 1 summarizes the conversions of azobenzene and the yields of products obtained by 4 h reaction. As shown by entry 1, the absence of catalyst scarcely promotes reaction. Addition of bare TiO₂ (entry 2) produces very small amounts of hydrazobenzene (2) and aniline (4). In contrast, as shown by entries 3-6, Pd_y/TiO₂ catalysts produce the secondary amine (N-benzylaniline, 1) with high yields. Among them, Pd_2/TiO_2 (entry 5) shows the highest activity, producing 1 with almost quantitative yield (98%). It is noted that the recovered Pd_2/TiO_2 catalyst, when reused for further photoreaction, shows almost the same activity as the fresh one. This suggests that the catalyst is reusable without the loss of activity and selectivity. As shown by entries 7 and 8, other metal particles such as Au and Pt, when loaded on TiO₂, produce 1 with very low yields ($\leq 6\%$). These findings clearly suggest that the Pd/TiO₂ catalyst specifically promotes the formation of secondary amine from alcohol and azobenzene.

Reaction mechanism

Secondary amine (1) is produced by tandem photocatalytic and catalytic actions on Pd/TiO₂ (Scheme 1): photoexcitation of TiO₂ produces the electron (e^-) and positive hole (h^+) pairs.

$$\mathrm{TiO}_2 + h \nu \to \mathrm{e}^- + \mathrm{h}^+ \tag{1}$$

The h⁺ oxidize alcohol and produces aldehyde and H⁺.¹⁷

$$R_1 - CH_2OH + 2h^+ \rightarrow R_1 - CHO + 2H^+$$
(2)

The e^- formed on the TiO₂ conduction band are transferred to the Pd particles. They reduce H⁺ and produce H atoms on the particle surface (H–Pd species).¹⁸

Table 1. Results for photoreaction of azobenzene and benzyl alcohol on the respective catalysts^a

$ \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & $											
entry	catalyst	diameter of metal particles / nm ^b	azobenzene conv. / %	Product yields / %							
				1 ^c	2 ^d	3 ^c	4 ^{<i>c</i>}				
1	none		0	0	0	0	0				
2	TiO ₂		15	0	7	0	8				
3	Pd _{0.5} /TiO ₂	2.6 ± 0.5	94	47	27	10	10				
4	Pd ₁ /TiO ₂	4.1 ± 0.9	>99	85	10	5	0				
5	Pd ₂ /TiO ₂	5.0 ± 0.9	>99	98	0	0	0				
	reuse		>99	98	0	0	0				
6	Pd ₄ /TiO ₂	6.5 ± 1.3	>99	68	0	20	12				
7	Au ₂ /TiO ₂	3.7 ± 0.5	25	2	12	4	4				
8	Pt ₂ /TiO ₂	3.1 ± 0.8	95	6	30	24	30				

^{*a*} Photoirradiation was carried out by a Xe lamp (500 W; light intensity at 300–400 nm, 27.2 W m⁻²). ^{*b*} Determined by TEM observations. TEM images of the catalysts and size distribution of metal particles are summarized in Fig. S1 (ESI†). ^{*c*} = [product formed (µmol)] / [initial amount of azobenzene (12.5 µmol) × 2] × 100. ^{*d*} = [product formed (µmol)] / [initial amount of azobenzene (12.5 µmol)] × 100.

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$$H^{+} + e^{-} + Pd \rightarrow H - Pd$$
 (3)

Azobenzene is reduced to two equivalents of anilines (4) by the surface H–Pd species,¹⁹ via the formation of a hydrazobenzene (2) intermediate.

$$R_2 - N = N - R_2 + 2H - Pd \rightarrow R_2 - NH - NH - R_2 (2) + 2Pd$$
 (4)

$$R_2-NH-NH-R_2(2) + 2H-Pd \rightarrow 2R_2-NH_2(4) + 2Pd$$
 (5)

Catalytic condensation of the formed aldehyde with aniline by the Lewis acid sites on the TiO_2 surface²⁰ produces imine (**3**).

$$R_{1}-CHO + R_{2}-NH_{2} \xrightarrow{\longrightarrow} R_{1}-CH=N-R_{2} (\mathbf{3}) + H_{2}O$$
(6)

The imine is hydrogenated by the H–Pd species to the product secondary amine (1).

$$R_1-CH=N-R_2(3) + 2H-Pd \rightarrow R_1-CH_2-NH-R_2(1) + 2Pd$$
 (7)

Fig. 1 shows the time-profiles for the amounts of substrate and products during reaction of azobenzene and benzyl alcohol on the Pd_2/TiO_2 catalyst. Decrease in the amount of azobenzene (black) associates with a formation of secondary amine (1, blue) and benzaldehyde (white). Photoreaction for 1.5 h produces 25 µmol 1, two equivalents of substrate azobenzene (12.5 µmol), indicating that two aniline units of azobenzene are quantitatively converted to 1. During reaction, hydrazobenzene (2, red), imine (3, green), and aniline (4, orange) are produced intermediately. These data suggest that 1 is indeed produced via the above reaction sequence (eqs. 2–7). In addition, prolonged irradiation (~3 h) does not affect the amount of 1, suggesting that further reaction of 1 does not occur.



Fig. 1 Time-dependent change in the amounts of substrate and products during photoreaction of azobenzene and benzyl alcohol on Pd_2/TiO_2 . The reaction conditions are identical to those in Table 1.

Effect of Pd loadings

As shown in Table 1 (entries 3–6), the Pd amount on TiO_2 strongly affects the activity for secondary amine formation. Pd_2/TiO_2 shows the highest activity, and the lower $(Pd_{0.5}, Pd_1)$ or higher Pd loading (Pd_4) catalysts show decreased activity.

Fig. S3 (ESI[†]) summarizes the time-profiles for the amounts of substrate and products during photoreaction on the respective catalysts. These data clearly reveal that the decreasing rates for the amounts of substrate azobenzene and all intermediates (2, 3, and 4) on the Pd_{0.5}, Pd₁, and Pd₄ catalysts are much lower than those on Pd₂/TiO₂ (Fig. 1). This suggests that slower reductions on these catalysts result in lower activity for secondary amine formation. As shown by eqs. 4, 5, and 7, the reduction reactions are promoted by the H-Pd species; therefore, the lower activity of these catalysts is probably due to the smaller number of H-Pd species formed. As shown by eqs. 2 and 3, the H-Pd species are produced via the oxidation of alcohol, and the number of H-Pd species depends on the amount of alcohol oxidized. To roughly determine the number of H-Pd species produced, a benzyl alcohol solution was photoirradiated with respective catalysts for 4 h without azobenzene. The amount of benzaldehyde formed is summarized in Fig. 2. The Pd₂/TiO₂ catalyst produces the highest amount of aldehyde, and the tendency for aldehyde formation is consistent with the activity for secondary amine formation (Table 1, entries 3-6). These data clearly suggests that Pd₂/TiO₂ produces the largest amount of H-Pd species and, hence, exhibits the highest activity for reduction reactions.





The smaller number of H–Pd species on lower Pd loading catalysts (Pd_{0.5}, Pd₁) is probably due to the insufficient charge separation of e^- and h^+ pairs, as often observed for related metal/semiconductor systems.²¹ In contrast, Pd₄/TiO₂ possesses a larger number of Pd atoms, but produces smaller number of H–Pd species. It is well known that a metal/semiconductor interface creates a Schottky barrier (ϕ_B), and its height increases with an increase in the amount of metal loaded.²² On Pd₄/TiO₂, the ϕ_B height increased by higher Pd loading may suppress smooth transfer of the conduction band e^- to Pd, probably resulting in insufficient charge separation. As a result of this, Pd₂/TiO₂ with appropriate Pd loading facilitates efficient charge separation and produces a larger number of H–Pd species, thus promoting efficient secondary amine formation.

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Table 2 Secondary amine synthesis from various alcohols and azobenzenes (R–N=N–R) on Pd₂/TiO₂^{ab}

run	alcohol	R-N=N-R	<i>t</i> / h	product	yield / % ^c
1	∕∩н	R= ~~~	1		99
2	∕∕он	~~~	1.5		99
3	~~он	~~~	1.5		99
4			1.5		98
5 ^d			24		91
6 ^e			6	N H	98
7 ^f			5		94
8 ^g			16		80
9		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	2		90
10	ОН	ОСН3	4	N N OCH3	95
11 ^g		~~~	8	C H OH	90
12 ^g		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	10	CN R	87
13		~~~	7	COOH	91
14 ^g		~~~ C I	5	N CI	38 ^h

^{*a*} Reaction conditions: azobenzenes (12.5 µmol), alcohols (0.5 mL, water (4.5 mL), catalyst (10 mg), Xe lamp ($\lambda > 300$ nm), light intensity at 300–400 nm (27.2 W m⁻²). ^{*b*} Conversions of azobenzenes in all runs are >99%. ^{*c*} = [product formed (µmol)] / [initial amount of azobenzene derivatives (µmol) × 2] × 100. ^{*d*} Azobenzene (62.5 µmol). ^{*e*} Catalyst (5 mg). ^{*f*} Light intensity at 300–400 nm (13.6 W m⁻²). ^{*g*} Catalyst (15 mg). ^{*h*} The yield of dehalogenated product (*N*-benzylaniline) is 55%.

Synthesis of various secondary amines

The Pd_2/TiO_2 catalyst is applicable for the synthesis of various types of secondary amines, as depicted in Table 2. Reactions of aliphatic alcohols and azobenzene (entries 1–3) produce the corresponding secondary amines with very high yields (99%), as is the case for the benzyl alcohol/azobenzene system (entry 4). As shown by entry 5, a large scale reaction also gave the product with high yield although relatively long reaction time is required. As shown by entries 6 and 7, decrease in the catalyst amount and the light intensity also prolongs the reaction time for secondary amine formation. This indicates that the catalyst amount and light intensity are very important factors for rapid secondary amine synthesis. As shown by entries 8–11, reactions

of 1,1'-azonaphthalene or azobenzenes bearing $-CH_3$, $-OCH_3$, and -OH groups also gave the products with high yields (\geq 80%). In addition, azobenzenes with reducible substituents such as -CN and -COOH groups (entries 12 and 13) are also successfully transformed to the secondary amines with high yields (\geq 87%) while maintaining the substituents as they are. It is noted that halogen-substituted azobenzene is unsuccessful for secondary amine synthesis: reaction of Cl-substituted azobenzene (entry 14) mainly gave a dechlorinated product because the H–Pd species also behave as the active site for dehalogenation.¹⁶ These results suggest that the Pd₂/TiO₂ catalyst is applicable for synthesis of several kinds of secondary amines, although some cases are unsuccessful owing to the subsequent reactions of substituents.

Conclusion

We found that photoexcitation of Pd/TiO₂ catalyst facilitates one-pot synthesis of secondary amines from alcohols and azobenzenes via consecutive photocatalytic and catalytic actions. As shown in Figure 1, the present system oxidizes large amount of alcohols because large amount of H atoms of alcohols are required for multi-step hydrogenation of substrates and intermediates (azobenzenes and imines). This negative aspect must be addressed for practical application by improvement of the process. Nevertheless, the present system offers several advantages: (i) easily recoverable and recyclable heterogeneous catalyst; (ii) mild reaction conditions (room temperature and atmospheric pressure); and, (iii) waste azobenzenes can be used as resources. The present system based on the consecutive photocatalytic and catalytic actions, therefore, have a potential to be a powerful method for one-pot green synthesis of secondary amines.

Experimental

Materials

All of the reagents used were supplied from Wako, Tokyo Kasei, and Sigma-Aldrich, and used without further purification. Water was purified by the Milli Q system. P25 TiO_2 (JRC-TIO-4) were kindly supplied from the Catalyst Society of Japan.

 Pd_x/TiO_2 catalysts [x (wt %) = $Pd/TiO_2 \times 100$; x = 0.5, 1, 2, 4] were prepared as follows: TiO_2 (1.0 g) and $Pd(NO_3)_2$ (10.9, 21.9, 44.2, or 90.2 mg) were added to water (40 mL), and the solvents were evaporated with vigorous stirring at 353 K for 12 h. The obtained powders were dried at 673 K under air flow (0.5 L min⁻¹) and then reduced at 673 K under H₂ flow (0.2 L min⁻¹). The heating rate and the holding time at 673 K for these treatments were 2 K min⁻¹ and 2 h, respectively. Pt_2/TiO_2 was prepared in a similar manner to Pd_x/TiO_2 with $H_2PtCl_6.6H_2O$ (54 mg) as a precursor.

 Au_2/TiO_2 was prepared by a deposition–precipitation method as follows:²³ HAuCl₄.4H₂O (45.8 mg) was added to water (50 mL). The pH of the solution was adjusted to 7 by an addition of 1 M NaOH. TiO₂ (1.0 g) was added to the solution Page 5 of 7

and stirred vigorously at 353 K for 3 h. The particles were recovered by centrifugation and washed with water. They were calcined at 673 K under an air flow (0.5 Lmin^{-1}) .

Photoreaction

Each of the respective catalysts (10 mg) was added to a mixture of water (4.5 mL) containing alcohol (0.5 mL) and azobenzene (12.5 µmol) within a Pyrex glass tube (20 cm³; ϕ 16.5 mm). The tube was sealed using a rubber septum cap and purged with N₂ gas. The tube was photoirradiated by a Xe lamp (500 W; Ushio Inc.) at $\lambda >$ 300 nm with magnetic stirring. The temperature of the solution during photoirradiation was ca. 303 K, and the light intensity was 18.2 W m⁻² (at 300–400 nm), respectively. After photoirradiation, the gas phase product was analyzed by GC-TCD (Shimadzu; GC-8A). The resulting solution was extracted with diethyl ether, and the obtained solution was analyzed by GC-FID (Shimadzu; GC-1700). The substrate and product concentrations were determined with authentic samples. Identification of the products was performed by a Shimadzu GC-MS system (GCMS-QP5050A).

Analysis

Total Pd amounts of the catalysts were determined by an X-ray fluorescence spectrometer (Seiko Instruments, Inc.; SEA 2110). Diffuse-reflectance UV–vis spectra were measured on an UV–vis spectrophotometer (Jasco Corp.; V-550 with Integrated Sphere Apparatus ISV- 469) with BaSO4 as a reference.²⁴ TEM observations were carried out using an FEI Tecnai G2 20ST analytical electron microscope operated at 200 kV.²⁵

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†Electronic Supplementary Information (ESI) available: Experimental details, supplementary data (Figs. S1–S3). See DOI: 10.1039/c000000x/

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- **Manuscript title:** Photocatalytic secondary amine synthesis from azobenzenes and alcohols on TiO₂ loaded with Pd nanoparticles
- Authors: Kaliyamoorthy Selvam, Hirokatsu Sakamoto, Yasuhiro Shiraishi,* and Takayuki Hirai

Graphical Abstract



Photoexcitation of TiO_2 loaded with Pd particles produces secondary amines from azobenzenes and alcohols with almost quantitative yields, via consecutive photocatalytic and catalytic actions.