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One-pot synthesis of imines from alcohols and amines with TiO₂ loading Pt nanoparticles under UV irradiation†

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TiO₂ loading Pt nanoparticles (Pt@TiO₂) promote one-pot synthesis of imines from alcohols and amines under UV irradiation at room temperature. This is achieved *via* a Pt-assisted photocatalytic oxidation of alcohols and a catalytic condensation of the formed aldehydes with amines on the TiO₂ surface.

Tandem catalysis that enables multi-step reactions in one pot has attracted much attention because it eliminates isolation of unstable intermediates and reduces waste production.[1] Various one-pot synthesis methods have been proposed, but many of these employ homogeneous catalysts, which generally suffer from product contamination and limited recyclability.[2] Design of heterogeneous catalytic systems that promote efficient one-pot synthesis is currently the focus of attention.[3]

Imines are an important class of chemicals that have been used for organic synthesis, pharmaceuticals, and agricultural chemicals.[4] Various methods for imine synthesis have been proposed based on the dehydrogenation of secondary amines, but most of them require stoichiometric amount of oxidants. Catalytic dehydrogenation methods have also been proposed using ruthenium complexes with dioxygen, iodosylbenzene, or quinone as oxidant;[5] however, they produce large amounts of byproducts. Recently, one-pot catalytic processes that produce imines directly from alcohols and amines were reported with manganese octahedral molecular sieves,[6] ruthenium hydroxide supported on TiO₂,[7] and palladium nanoparticles supported on boehmite nanofibers;[8] however, these require relatively high reaction temperatures (> 363 K). To the best of our knowledge, there is only one heterogeneous catalytic system that promotes one-pot imine synthesis under mild conditions (333 K), employing gold nanoparticles supported on hydroxyapatite.[9]

Here we report a new catalytic system that promotes one-pot imine synthesis at room temperature. We use TiO₂ loading platinum particles (Pt@TiO₂) under UV irradiation ($\lambda > 300$ nm). This promotes two different transformations in

one pot by photocatalytic and catalytic actions: the conversion of alcohol to aldehyde *via* a Pt-assisted photocatalytic oxidation on the TiO₂ surface; and a condensation of amine with the formed aldehyde on the Lewis acid site on the TiO₂ surface. Several reports describe the photocatalytic condensation of alcohols and nitrogen-containing compounds;[10] however, none of the systems achieve selective imine formation.

Pt(x)@TiO₂ with different Pt loadings [x (wt%) = Pt/(Pt + TiO₂) × 100] were prepared with JRC-TIO-4 TiO₂ (equivalent to Degussa P25; average particle diameter 23.7 nm (Fig. S1, ESI†); supplied by the Catalyst Society of Japan) by impregnation of H₂PtCl₆ followed by reduction with H₂ (ESI†).[11] A transmission electron microscopy (TEM) image of Pt(0.3)@TiO₂ shows spherical Pt particles with an average diameter of 1.8 nm (Fig. 1). The lower or higher Pt loadings create smaller or larger Pt particles; $x = 0.1$ and 1.0 catalysts have 1.3 and 2.2 nm particles, respectively (Fig. S2, ESI†). Diffuse reflectance UV-vis spectra reveal that the catalysts with higher Pt loadings show an increased absorbance at > 300 nm due to the light scattering by the Pt particles (Fig. S3, ESI†), although the band gap energies of the catalysts are similar (3.1–3.2 eV).

Table 1 summarizes the results of *N*-benzylidenaniline (**1**) synthesis by photoirradiation ($\lambda > 300$ nm, 12 h) of a benzyl alcohol solution (5 mL) containing aniline (10 mM) with respective catalysts (5 mg) under N₂ (ESI†). With pure TiO₂ (run 1), the yield of **1** is only 2%. In contrast, Pt(x)@TiO₂ show much higher yields (runs 2–7). In particular, $x = 0.3$ catalyst (run 5) shows the highest yield (97%) with a hydrogenated compound of **1**, *N*-benzylphenylamine (**2**), scarcely formed (3%), which barely increases even after prolonged

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Fig. 1 (a) TEM image of fresh Pt(0.3)@TiO₂ and (b) size distribution of Pt particles on (white) the fresh catalyst and (black) the catalyst recovered after 2nd reuse for the reaction (Table 1, run 9).

Table 1 Results of one-pot synthesis of N-benzylideneaniline with various catalysts under UV irradiation[a]
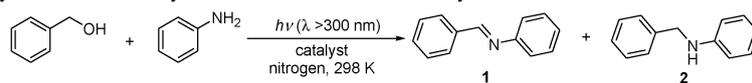
Run	Catalyst	Aniline conv.[b] (%)	Yields[b] (%) 1	2	Benzaldehyde formed[b]/μmol	H_2 formed[b]/μmol	Ti–OH_2^+ amount[c]/μmol
1	TiO_2	2	2	0	3	5	<1
2	Pt(0.05)@TiO_2	79	76	3	81	119	<1
3	Pt(0.1)@TiO_2	89	84	5	86	126	4
4	Pt(0.2)@TiO_2	91	87	4	105	144	9
5	Pt(0.3)@TiO_2	>99	97	3	136	179	11
6	Pt(0.5)@TiO_2	54	48	6	167	183	16
7	Pt(1.0)@TiO_2	42	36	6	192	192	36
8[d]	Pt(0.3)@TiO_2	>99	97	3			
9[e]	Pt(0.3)@TiO_2	>99	96	4			

[a] Reaction conditions: benzyl alcohol, 5 mL; aniline, 50 μmol; catalyst, 5 mg; N_2, 1 atm; temperature, 298 K; photoirradiation time, 12 h. [b] Determined by GC. [c] = [{(benzaldehyde formed) + (aniline converted)} − {(H_2 formed) + (**2** formed)}] × 2, where free H^+ in solution is negligible because the absorption analysis with methyl orange as a H^+ indicator does not detect free H^+ in solution. [d] 1st reuse of the catalyst (run 5) after water washing. [e] 2nd reuse.
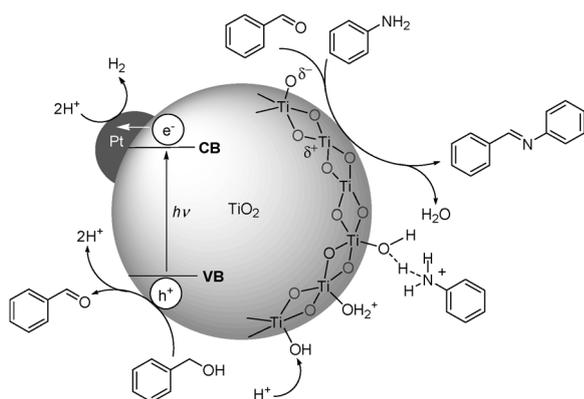
Scheme 1 Proposed pathway for the imine formation on Pt@TiO_2.

photoirradiation (Fig. S4, ESI†). These findings suggest that the present system enables direct imine production, while suppressing hydrogenation.

The imine is produced by tandem photocatalytic and catalytic reactions on Pt@TiO_2 (Scheme 1). The reaction is initiated by photoexcitation of TiO_2, producing electron (e^-) and positive hole (h^+) pairs. The h^+ oxidizes alcohol to aldehyde. Catalytic condensation of the formed aldehyde and amine on the Lewis acid site on TiO_2 produces imine.[12] The imine formation enhancement with the Pt loadings at 0.05–0.3% (runs 2–5) is because the Pt particles trap e^- on the excited TiO_2 and enhance the charge separation between e^- and h^+.[13] This accelerates aldehyde formation and, hence, facilitates condensation. The amounts of benzaldehyde and H_2 formed increase with the Pt loadings (Table 1), indicating that e^- trapped by the Pt particles are consumed by reduction of protons (H^+), which are produced by photocatalytic oxidation of alcohol (Scheme 1).

The catalytic condensation of aldehyde with amine on the Lewis acid site of TiO_2[12] is confirmed by the reaction of aniline with 1.5 equiv. of benzaldehyde in the dark at 298 K. As shown in Fig. 2a (white), the absence of catalyst gives **1** with 26% yield, while the presence of TiO_2 or Pt@TiO_2 shows >93% yield, indicating that all these catalysts promote
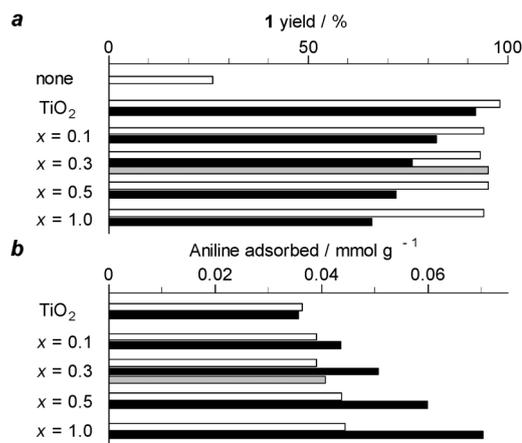

Fig. 2 (a) Yield of **1** during reaction of benzaldehyde (75 μmol) and aniline (50 μmol) in benzyl alcohol (5 mL) at 298 K for 6 h in the dark with (white) fresh catalysts and (black) the catalysts after UV irradiation (5 mg). (b) Amount of aniline adsorbed during adsorption experiments of aniline (0.5 mM) in benzyl alcohol (5 mL) at 298 K for 3 h with (white) fresh catalysts and (black) the catalysts after UV irradiation (5 mg). The catalysts (5 mg) were irradiated by UV light in benzyl alcohol (5 mL) for 3 h under N_2. They were washed with benzyl alcohol and used for experiments. The gray bars are the results of UV-irradiated Pt(0.3)@TiO_2 catalyst when used after water washing.

condensation. However, as shown in Table 1 (runs 6 and 7), the catalysts with higher Pt loadings ($x > 0.5$) show a much lower yield of **1**, although a larger amount of benzaldehyde is produced by the Pt-assisted photocatalytic oxidation. This is because these catalysts produce a larger amount of H^+. These H^+ are not only reduced on the Pt surface but also react with the surface –OH groups on TiO_2, producing the Brønsted acid site (Ti–OH_2^+).[14] Protonation of amines by the Ti–OH_2^+ species reduces the nucleophilicity of amines and suppresses the condensation (Scheme 1).[15]

The formation of Ti–OH_2^+ during photoirradiation is confirmed by a temperature-programmed desorption (TPD) analysis with NH_3 (Fig. S5, ESI†): fresh Pt@TiO_2 catalysts do not desorb NH_3 at >750 K, but the catalysts when irradiated

Table 2 One-pot imine synthesis from various alcohols and amines[a]

$$R_1\text{—OH} + R_2\text{—}\langle\text{—}NH_2 \xrightarrow[\substack{\text{catalyst}\\ \text{nitrogen, 298 K}}]{h\nu\,(\lambda > 300\ nm)} R_1\text{—}N\text{—}\langle\text{—}R_2$$
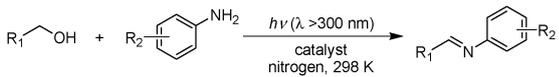
Run	R_1	R_2	t/h	Catalyst	Amine conv.[b] (%)	Yield[b] (%)
1	Methyl	H	2	TiO$_2$	16	14
2				Pt(0.3)@TiO$_2$	90	80
3	n-Propyl		2	TiO$_2$	12	11
4				Pt(0.3)@TiO$_2$	91	86
5	Cyclohexyl		16	TiO$_2$	16	14
6				Pt(0.3)@TiO$_2$	91	84
7	Ph	2-Me	16	TiO$_2$	5	4
8				Pt(0.3)@TiO$_2$	>99	97
9		3-Me	12	TiO$_2$	12	2
10				Pt(0.3)@TiO$_2$	>99	91
11		4-Me	12	TiO$_2$	7	6
12				Pt(0.3)@TiO$_2$	94	86
13		4-MeO	16	TiO$_2$	15	14
14				Pt(0.3)@TiO$_2$	>99	83
15[c]		4-Cl	4	TiO$_2$	12	11
16[c]				Pt(0.3)@TiO$_2$	83	74

[a] Reaction conditions: alcohol, 5 mL; amine, 50 µmol; catalyst, 5 mg; temperature, 298 K; N$_2$, 1 atm. [b] Determined by GC. [c] Amine, 20 µmol.

by UV light in benzyl alcohol show a distinctive desorption profile assigned to the Brønsted acid site.[16] The desorbed amount of NH$_3$ increases with the Pt loadings, indicating that higher Pt loadings produce larger amounts of Ti–OH$_2^+$. As shown in Table 1, the amount of Ti–OH$_2^+$, roughly determined from the mass balance of H$^+$, increases with the Pt loadings. This supports the formation of larger amounts of Ti–OH$_2^+$ on the catalysts with higher Pt loadings.

The protonation of amine by Ti–OH$_2^+$ is confirmed by the adsorption experiments of aniline with catalysts at 298 K. As shown in Fig. 2b (white), the fresh catalysts show similar aniline adsorption. In contrast, the catalysts, when irradiated by UV light (black), show an increased adsorption with the Pt loadings, indicating that aniline is protonated by Ti–OH$_2^+$. In addition, as shown in Fig. 2a (black), the UV-irradiated catalysts, when used for condensation of aniline with benzaldehyde, show a decreased yield of **1** with the Pt loadings. These indicate that the catalysts with higher Pt loadings produce larger amounts of Ti–OH$_2^+$ during UV irradiation, which promotes the protonation of amines and suppresses the condensation.[17] Efficient imine synthesis, therefore, requires a catalyst with an appropriate Pt loading (0.1–0.3%) that promotes efficient photooxidation of alcohols while producing a smaller amount of Ti–OH$_2^+$.

It is noted that the Ti–OH$_2^+$ species are deprotonated by simple water washing of catalysts.[14] Upon water washing (Fig. 2, gray), the UV-irradiated Pt(0.3)@TiO$_2$ shows high activity for condensation of aldehyde with aniline (Fig. 2a) and a low adsorption amount of aniline (Fig. 2b) similar to those of the fresh catalyst. This indicates that accumulation of Ti–OH$_2^+$ is suppressed by water washing. As shown in Table 1 (runs 8 and 9), Pt(0.3)@TiO$_2$, when washed with water, is reusable for imine synthesis at least two times without loss of activity and selectivity. In addition, TEM analysis of the catalyst recovered after the reaction reveals that the Pt particle size scarcely changes during reaction (Fig. 1b).

The tandem reactions promoted on Pt@TiO$_2$ are tolerant for synthesis of various substituted imines (Table 2). UV irradiation of alkyl or benzyl alcohols containing various kinds of aromatic amines with Pt(0.3)@TiO$_2$ produces the corresponding imines with high yields (>74%).[18]

In summary, we found that UV irradiation of Pt@TiO$_2$ achieves one-pot imine synthesis. This simple system offers significant advantages: (i) no harmful byproduct; (ii) the reaction proceeds at room temperature; and (iii) most of the hydrogen atoms removed by alcohol oxidation are recovered as H$_2$ gas, a clean energy resource. The system therefore has potential as a sustainable method for imine synthesis.

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17 The amount of Lewis acid site on Pt@TiO$_2$ scarcely decreases. As shown in Fig. S4, ESI†, the NH$_3$ desorption peak at *ca.* 500 K, assigned to the Lewis acid site (ref. 16a), scarcely changes even after UV irradiation in benzyl alcohol. This again suggests that the Ti–OH$_2^+$ species suppress the imine formation.

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