

Selective Amine Oxidation Using Nb₂O₅ Photocatalyst and O₂

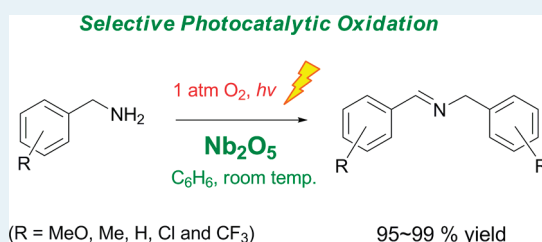
Shinya Furukawa, Yasuhiro Ohno, Tetsuya Shishido,* Kentaro Teramura, and Tsunehiro Tanaka*

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

Supporting Information

ABSTRACT: Niobium oxide (Nb₂O₅) can function as a photocatalyst for selective oxidation of benzylamine rather than other semiconductor metal oxides such as TiO₂, ZnO, and WO₃. Various amines including primary, secondary, and cyclic amines are also photocatalytically converted to corresponding imines in excellent yields by using Nb₂O₅ in an atmospheric pressure of O₂. Nb₂O₅ exhibits a catalytic activity with high selectivity even under visible light ($\lambda > 390$ nm) irradiation, although Nb₂O₅ does not absorb visible light.

KEYWORDS: amine oxidation, photocatalyst, niobium oxide, selective oxidation, aerobic oxidation



Oxidation of amine to imine is an important chemical transformation because of the versatile applications of imines as synthetic intermediates of medicines or biologically active nitrogen containing organic compounds.¹ Several oxidation procedures using stoichiometric oxidants such as 2-iodoxybenzoic acid^{2,3} or *N*-*tert*-butylphenylsulfonimidoyl chloride⁴ have been reported. However, a catalytic system using molecular oxygen as a sole oxidant has been desired in view of green chemistry.^{5,6} In this context, a number of transition-metal catalyzed aerobic oxidation systems have been developed. Ru-based catalysts such as RuCl₃,⁷ [RuCl₂(RCH₂NH₂)₂(PPh₃)₂],^{8,9} Ru-porphyrin,¹⁰ Ru-hydroxyapatite,¹¹ Ru₂(OAc)₄Cl,¹² and Ru/Al₂O₃¹³ are known to be effective for aerobic oxidation of amines. Au nanoparticles supported on Al₂O₃,^{14,15} CeO₂,^{14,15} graphite,¹⁶ and hydroxyapatite¹⁶ are also found to be good catalysts for amine oxidation. But in these systems, expensive precious metals are employed and relative high temperature (mostly >373 K) is required.

Utilizing semiconductor photocatalysts for aerobic oxidation of organic molecules has practical advantages of economical efficiency, environmental-friendliness, reusability, and durability. In addition, to effectively utilize solar energy, it is necessary to develop a material that will function under visible light.¹⁷ Very recently, Su and co-workers reported that mesoporous graphite carbon nitride (mpg-C₃N₄) can work as effective photocatalyst to activate O₂ for the selective oxidations of benzylic alcohols and amines with visible light.^{18,19} Although this material exhibits excellent catalytic performance under visible light irradiation, high oxygen pressure (0.5 MPa) and trifluorotoluene as solvent are necessary to obtain good yields. Zhao et al. reported that photooxidation of amines using TiO₂ with UV light gave a high selectivity to imines under a diluted condition.²⁰ We recently reported that photocatalytic oxidation of various alcohols proceeded selectively over niobium oxide (Nb₂O₅) under a mild condition.^{21,22} Nb₂O₅ showed higher selectivities to partial oxidation products; therefore, it can be thought that Nb₂O₅ is more suitable for selective oxidation than TiO₂. Moreover, we found that Nb₂O₅ can catalyze the selective photooxidation of alcohols even under visible light

Table 1. Oxidation of Benzylamine over Various Metal Oxides^a

entry	catalyst	yield (μ mol)	yield (μ mol/mmol cat) ^b	selectivity (%) ^c
1	TiO ₂	886	708	89
2	ZnO	790	643	94
3	Nb ₂ O ₅	649	915	98
4 ^d	Nb ₂ O ₅	n. d.		
5	MoO ₃	328	472	97
6	CeO ₂	264	497	97
7	Ta ₂ O ₅	201	444	96
8	ZrO ₂	175	216	95
9	WO ₃	143	332	89
10	V ₂ O ₅	322	298	59 ^e
11	none	199		81

^a Reaction conditions: catalyst (100 mg), benzylamine (5 mmol), benzene as a solvent (10 mL), irradiation time (5 h), oxygen pressure (1 atm).

^b Amount of *N*-benzylidene benzylamine per mole of catalyst. ^c Selectivity to *N*-benzylidene benzylamine. Benzaldehyde was yielded as a main byproduct except entry 10. ^d In the dark. ^e Benzylamine-*N*-carbaldehyde was formed as a main byproduct.

irradiation up to 450 nm, although the band gap of Nb₂O₅ is at 390 nm (3.2 eV).

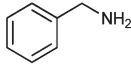
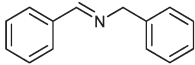
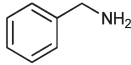
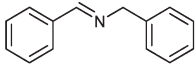
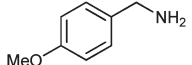
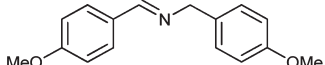
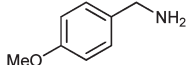
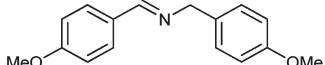
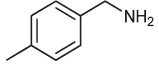
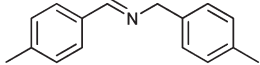
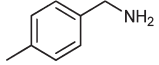
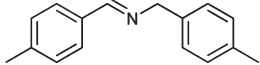
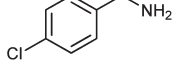
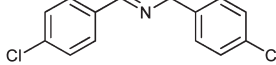
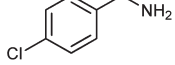
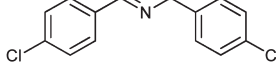
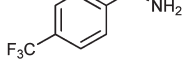
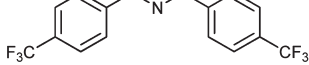
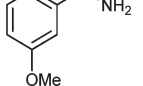
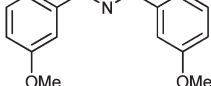
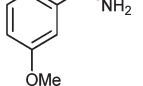
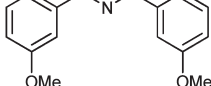
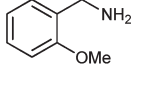
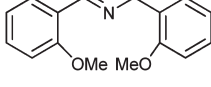
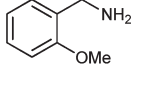
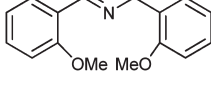
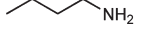
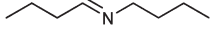
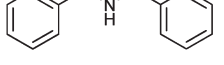
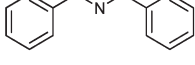
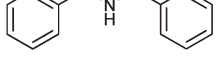
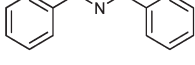
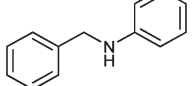
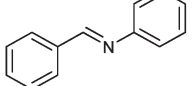
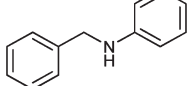
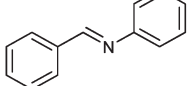
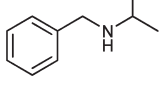
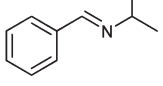
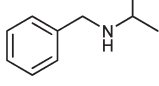
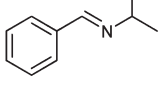
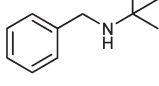
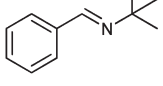
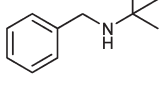
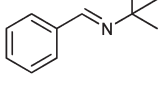
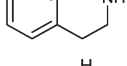
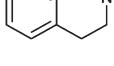
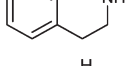
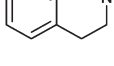
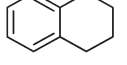
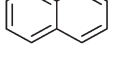
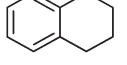
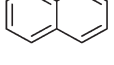
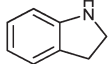
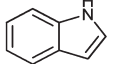
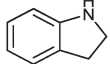
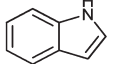
In the present study, we report that photocatalytic aerobic oxidations of various benzylic amines to imines take place over Nb₂O₅ with high yields at room temperature and atmospheric pressure. Nb₂O₅ exhibits a catalytic activity in high selectivity even under visible light irradiation as well as alcohol oxidation.

Received: June 14, 2011

Revised: August 11, 2011

Published: August 15, 2011

Table 2. Aerobic Oxidation of Various Amines to Corresponding Imines Using Nb₂O₅^a

Entry	Substrate	Product	T / h	Conv. (%)	Sel. (%) ^b
1			50	>99	97
1'			24	21	97
				0 ^c	– ^c
2			24	>99	99
2'			24	29	94
3			38	>99	95
3'			24	19	94
4			45	>99	98
4'			24	12	94
5			51	>99	96
6			27	>99	95
6'			24	30	95
7			29	>99	94
7'			24	16	95
8			24	>99	61(14) ^d
9			20	97	71 (23)
9'			24	16	70 (29)
10			48	15	63 (21)
10'			24	2.5	86 (9)
11			15	82	92 (5)
11'			24	47	91 (5)
12			24	30	88 (7)
12'			24	13	89 (8)
13			11	>99	92 (5) ^e
13'			24	47	85 (6) ^e
14			48	43	70 (4, 20) ^{f,g}
14'			24	4.2	84 (8) ^g
15			24	39	64 (13, 14) ^{h,i}
15'			24	2.4	87 (12) ^h

^a Reaction condition: Nb₂O₅ (100 mg), substrate (5 mmol), benzene as a solvent (10 mL), $\lambda > 300$ nm (entries 1–15) or $\lambda > 390$ nm (entries 1'–15'), oxygen pressure (1 atm). ^b Selectivities to corresponding imines. Figures in parentheses show selectivities to benzaldehyde. ^c Without catalyst.

^d Selectivities to *N,N*-dibutylformamide. ^e Selectivities to isoquinoline. ^f Selectivities to 3,4-dihydroquinoline. ^g Selectivities to 3,4-dihydroquinoline-1(2*H*)-carbaldehyde. ^h Selectivities to indoline-1-carbaldehyde. ⁱ Selectivities to 10,11-dihydro-5*H*-dibenzo[*b,f*]azepine, respectively.

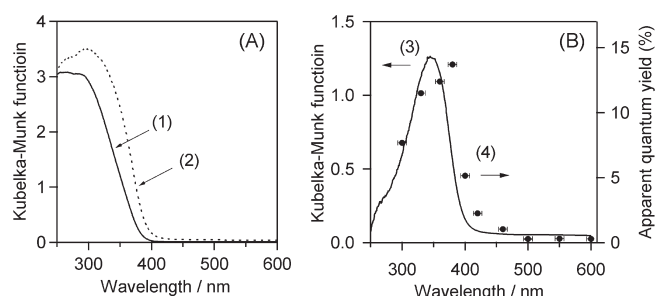
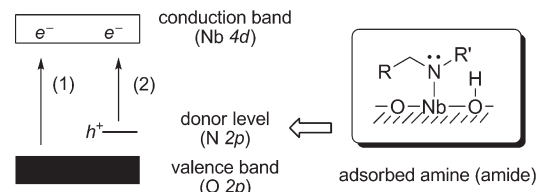


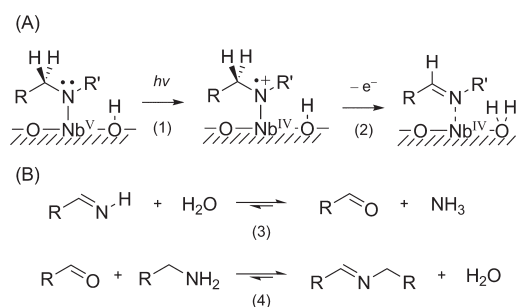
Figure 1. (A) UV-vis spectra of (1) Nb₂O₅, and (2) Nb₂O₅ with adsorbed benzylamine. (B) (3) Differential UV-vis spectrum of (2) - (1), and (4) action spectrum of benzylamine photooxidation over Nb₂O₅.

Photocatalytic activity and selectivity in the aerobic oxidation of benzylamine over various metal oxides are summarized in Table 1. TiO₂, ZnO, and Nb₂O₅ show much higher yields of *N*-benzylidene benzylamine than other oxides (Table 1, entry 1–3). Nb₂O₅ showed the highest yield per mole of catalyst (Table 1, entry 3). TiO₂, which is an extensively used photocatalyst, also exhibited higher yield than Nb₂O₅ and ZnO. However the selectivity to *N*-benzylidene benzylamine was comparatively low because benzaldehyde was formed as a byproduct (Table 1, entry 1). The highest selectivity was obtained with Nb₂O₅ among the metal oxides tested. When benzylamine was photoirradiated in the absence of any catalyst, a very low yield was observed (Table 1, entry 11). The evolution of photogenerated products over Nb₂O₅ responded to illumination. Moreover, no product was detected in the dark with the Nb₂O₅ catalyst (Table 1, entry 4). These indicate that the photooxidation over the Nb₂O₅ catalyst was due entirely to a photocatalytic reaction. The oxidation of various amines including primary, secondary, and bicycloamine derivatives were examined by using the Nb₂O₅ photocatalyst (Table 2). Primary benzylamine derivatives bearing various functional groups (OMe, Me, H, Cl, and CF₃) were converted to corresponding coupled imines with excellent yields (Table 2, entries 1–7). Electron-rich benzylamines (OMe and Me derivatives) were oxidized faster than electron-deficient ones (Cl and CF₃ derivatives) (Table 2, entries 2–5). The reaction rate of the regioisomer increased in the order of *ortho* < *meta* < *para* isomer, indicating the presence of a steric effect (Table 2, entries 2, 6, and 7). A primary aliphatic amine was also converted to the corresponding coupled imine, but the selectivity was lower than those of benzylic homologues (Table 2, entry 8). Secondary *N*-alkylbenzylamines (alkyl = Bn, Ph, *i*Pr, and *t*Bu) were also oxidized to dehydrogenated imines. (Table 2, entries 9–12). Relative high yields were observed within 20 h in the oxidations of *N*-isopropylbenzylamine and dibenzylamine. On the other hand, *N*-phenyl and *N*-*tert*-butyl derivatives were oxidized very slowly. The order of reaction rates corresponding to the bulkiness of the alkyl moiety (*i*Pr > Bn ≫ *t*Bu > Ph) indicates that steric hindrance around the nitrogen atom is a key factor for the reaction rate. Benzaldehyde was formed as a byproduct in the oxidations of these secondary benzylic amines. The formation of benzaldehyde is attributed to the oxidative cleavage of the C–N bond. In addition, a small amount of *N*-benzylidene benzylamine was also yielded in these cases. This represents an involvement of the C–N bond cleavage, followed by coupling of the fragments. 1,2,3,4-Tetrahydroisoquinoline was smoothly converted to monodehydrogenated 3,4-dihydroisoquinoline with high yield (Table 2, entry 13). In contrast, the rate of oxidation of 1,2,3,4-tetrahydroquinoline to

Scheme 1. Schematic Illustration of Photo-Induced Electron Excitation: (1) Band Gap Excitation of Nb₂O₅ and (2) Excitation from a Donor Level Derived from Adsorbed Amine Species



Scheme 2. Proposed Mechanisms of (A) Dehydrogenation of Amine, (1) Charge Separation, (2) Imine Formation; and (B) Dimerization of Amine, (3) Hydrolysis of a Primary Imine, (4) Condensation of Amine and Aldehyde



aromatized quinoline was much slower than the *iso*-isomer (Table 2, entry 14). In this case, a small amount of monodehydrogenated 3,4-dihydroquinoline as an intermediate product was also detected. The significant difference of the reaction rate between the tetrahydroquinoline isomers is generally observed in various catalytic systems.^{12,16,19,23} Indole was yielded with moderate selectivity in the oxidation of indoline. The Nb₂O₅ photocatalyst was reusable and showed the same conversion and selectivity without any pretreatment as the catalyst as prepared (see Supporting Information, Figure S1).

The amine oxidations over Nb₂O₅ took place even under visible light (>390 nm) irradiation (Table 2, entries 1'–15'). Although the reaction rates were lower than that under UV (>300 nm) irradiation, comparable selectivities were obtained. In the absence of Nb₂O₅, oxidation of benzylamine did not proceed under visible irradiation (Table 2, entry 1'). Nb₂O₅ shows an intense broad band at 300 nm because of band gap excitation, but no absorption in the region of $\lambda > 390$ nm (Figure 1A, trace 1). Indeed, the apparent quantum yield as a function of the wavelength of the incident light (action spectrum) does not agree with the UV-vis spectrum of Nb₂O₅, and the reaction is responsive to light up to 460 nm (Figure 1B, plot 4). Therefore, this result indicates that the photoactivation mechanism of amine over Nb₂O₅ is different from the classical electron transfer mechanism found in semiconductor photocatalysis: the formation of an excited electron in the conduction band and of the positive hole in the valence band. We previously reported an analogous phenomenon; alcohol oxidation over Nb₂O₅ took place under visible light (>390 nm) irradiation. By means of UV-vis, electron spin resonance (ESR), and FT/IR studies, the detailed reaction mechanism of alcohol photooxidation was revealed, and a unique

photoactivation mechanism by “*in situ doping*” was proposed, that is, the direct electron transfer from the O 2p orbital derived from adsorbed alcoholate species to the conduction band consisting of Nb 4d orbitals.^{22,24} In a similar fashion, amine oxidation over Nb₂O₅ with visible light may be attributed to a direct electron transfer from a donor level consisting of a N 2p orbital derived from adsorbed amine species (Scheme 1). Figure 1A, trace 2 shows the UV–vis spectrum obtained when benzylamine was added to Nb₂O₅. The absorption band at 300 nm extended to a higher wavelength region, and the differential spectrum before and after the adsorption of benzylamine showed a new absorption band at about 350 nm which was overlapped with the region of >390 nm (Figure 1B, trace 3). Since benzylamine itself exhibits no absorption in the region of >300 nm (See Supporting Information, Figure S2), the new absorption is ascribed to the surface complex consisting of adsorbed amine species and Nb₂O₅. Moreover, the differential spectrum shows a good agreement with the action spectrum. These results strongly suggest that the amine oxidation is triggered by light absorption by the surface complex consisting of adsorbed amine species and Nb₂O₅, in other words, direct electron excitation from the donor level derived from adsorbed amine species.

On the basis of these results, we propose a possible reaction mechanism as shown in Scheme 2A. At first, dissociative adsorption of amine forms an amide (RR'N–Nb) species. The electron excitation from the N 2p orbital of dissociatively adsorbed amine species (amide) to the conduction band results in the formation of an amide radical cation and reduced Nb(IV) (Step (1)). This radical cation intermediate is further oxidized to imine, and the electron is trapped to the other Nb(V) site (Step (2)). Then, the reduced Nb(IV) sites are reoxidized to Nb(V) by molecular oxygen. The proposed mechanism is essentially the same as that of alcohol photooxidation over Nb₂O₅.²² The photoactivation of amine is supposed to be more favorable than that of alcohol because of its donating ability. However, detailed the reaction mechanism is now under investigation and will be reported in the near future.

In the oxidation of benzylamine, a corresponding primary imine was not detected. On the other hand, ammonia and benzaldehyde in addition to *N*-benzylidene benzylamine were observed, indicating that the hydrolysis of a primary imine took place. Moreover, when benzaldehyde was added to benzylamine in the absence of Nb₂O₅ in the dark, the condensation of benzaldehyde and benzylamine to *N*-benzylidene benzylamine immediately and quantitatively proceeded. These results indicate that a rapid dimerization takes place regardless of catalyst and photoirradiation; the produced primary imine is hydrolyzed to aldehyde and ammonia, followed by condensation of the aldehyde and the primary amine (Steps (3) and (4) in Scheme 2B).^{14,16}

In conclusion, Nb₂O₅ can act as an efficient heterogeneous photocatalyst for the aerobic oxidation of various amines to the corresponding imines under atmospheric pressure at room temperature. This reaction takes place even under visible irradiation up to about 460 nm although the band gap of Nb₂O₅ is 390 nm.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details, recycle test, and UV–vis spectrum of benzylamine. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: shishido@moleng.kyoto-u.ac.jp (T.S.), tanakat@moleng.kyoto-u.ac.jp (T.T.).

Funding Sources

This work was partially supported by Grants-in-Aid for Scientific Research on Priority Areas (No. 17034036, “Molecular Nano Dynamics” and No. 20037038, “Chemistry of Concerto Catalysis”) and Scientific Research (No. 19360365, “B”) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. K.T. is supported by the Program for Improvement of Research Environment for Young Researchers from Special Coordination Funds for Promoting Science and Technology (SCF) commissioned by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. T.S. acknowledges the Research Seeds Quest Program (Lower Carbon Society) (2010) under Japan Science and Technology Agency. S.F. thanks the JSPS Research Fellowships for Young Scientists.

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