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Selective Aerobic Oxidation of Primary Alcohols to Aldehydes over Nb_2O_5 Photocatalyst with Visible Light

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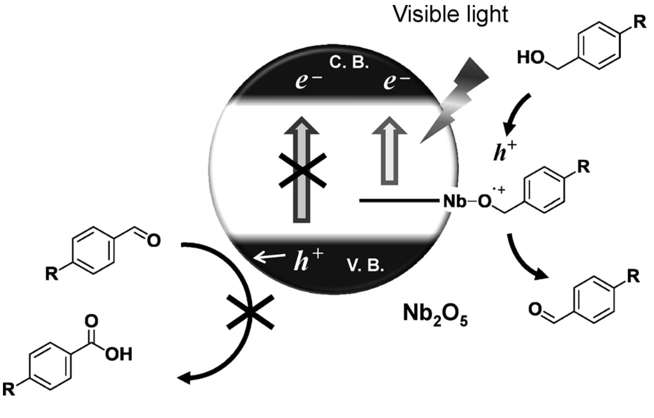
Primary alcohols are selectively converted into aldehydes by using a Nb_2O_5 photocatalyst under visible-light irradiation. A strong interaction between the alcohol and Nb_2O_5 generates a donor level within the forbidden band of Nb_2O_5, which provides a visible-light-harvesting ability. Over oxidation of aldehydes into carboxylic acids does not proceed under visible-light irradiation.

Oxidation of alcohols to corresponding carbonyl compounds is one of the most important chemical conversions in industrial processes and organic synthesis. In the principle of green chemistry, development of a system that is catalytic and employs an environmentally friend oxidant is desired.[1] Catalytic aerobic oxidation has been one of the most effective systems for alcohol oxidation. Several heterogeneous catalytic systems that use noble-metal elements (Au,[2] Ag,[3] Pd,[4] and Ru[5]) have been reported as effective catalysts for the aerobic oxidation of alcohols. However, replacement of the noble metals to non-precious and abundant materials is necessary in terms of economic efficiency and ubiquitous element strategy. In this context, heterogeneous photocatalytic systems have a number of advantages such as reusability, durability, economical efficiency, and utilization of solar energy. Selective photooxidation of alcohols to the corresponding carbonyl compounds by using molecular oxygen has been a hot topic.[6]

In general, aerobic photooxidation of alcohols can proceed by two different pathways. One is a hole-derived pathway, in which a positive hole that is trapped at a lattice oxygen (O^-) and/or other active oxygen species, such as an ozonide anion radical (O^{3-}) or a hydroxyl radical ($HO^{\bullet}$), triggers the oxidation. This pathway involves undesired deep oxidation of the produced carbonyl compounds into CO_2, owing to the strong oxidation abilities of the oxidizing species.[7] The other pathway is an electron-derived path way, in which a superoxide anion radical (O^{2-}) formed through the reduction of a molecular oxygen with an excited electron triggers the oxidation.[8] This process provides greater selectivity towards the carbonyl compounds compared to the hole-derived pathway, partly because the oxidizing ability of O^{2-} is milder than the hole-derived active oxygen species.[9] In the oxidation of primary alcohols, however, over oxidation of the produced aldehydes into carboxylic acid often occurs,[8] because aldehydes are more easily oxidized than alcohols. Thus, the selective photooxidation of primary alcohols into aldehydes is challenging and requires a novel strategy that overcomes such an over oxidation. Recently, Tanaka et al. reported that the photocatalytic oxidation of primary alcohols to aldehydes selectively proceeded over Au/CeO_2.[10] They also suggested that the active oxygen species were being removed in the reaction system and implied an involvement of Au in the removal.

We recently demonstrated that the photooxidation of alcohols proceeds over Nb_2O_5 through a unique photoactivation mechanism that differs from the classical bandgap excitation mechanism. Excitation from a donor level consisted of an O 2p orbital, localized at the alcoholic oxygen, binding to a Nb site in the conduction band of Nb_2O_5 (Scheme 1).[11]

A similar mechanism has been proposed in the photooxidation of an amine to an imine over Nb_2O_5.[12] This photoexcitation style has the unique properties as follows: 1) its excitation energy is smaller than the bandgap energy of Nb_2O_5 and



Scheme 1. Photoexcitation of alcohol oxidation over Nb_2O_5. A strategy for the selective oxidation of primary alcohols to aldehydes is also illustrated.

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reaches the visible region (< 3.2 eV); 2) the reaction proceeds with visible light, even though the bandgap energy of Nb_2O_5 is larger than 3.2 eV; 3) the localized excitation only enables the formation of a positive hole at the alcoholic oxygen and not at the lattice oxygen that causes the over oxidation. In this context, it is expected that visible-light irradiation of Nb_2O_5 in the presence of an alcohol excludes the bandgap excitation of Nb_2O_5 itself and causes the localized excitation selectively, leading to the selective photooxidation of the alcohol to the aldehyde (Scheme 1).

Figure 1 shows the time course of the product yield in the aerobic photooxidation of *p*-methoxybenzylalcohol over Nb_2O_5 under the irradiation of UV/Vis (> 300 nm) and visible (> 390 nm) light.

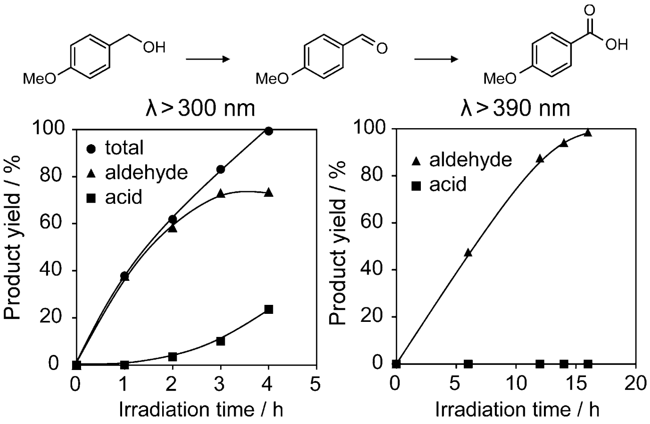
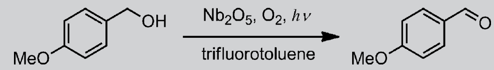


Figure 1. Time course of the product yields in the aerobic photooxidation of *p*-methoxybenzylalcohol over Nb_2O_5 under irradiation of a) UV/Vis (> 300 nm) and b) visible (> 390 nm) light.

In the presence of UV light, *p*-methoxybenzaldehyde was yielded as the main product at the initial stage, whereas over oxidation of the aldehyde to the corresponding carboxylic acid occurred considerably at the end of the reaction. In contrast, under the irradiation of visible light (in the absence of UV light), the aldehyde was obtained exclusively, even at 99% conversion of the alcohol. It took a longer reaction time to reach 99% conversion under visible-light irradiation than under UV/Vis light, which was probably because of the decrease in the number of photons by using an L-42 cutoff filter. Table 1 shows the results of several control experiments. Replacement of the reaction atmosphere from O_2 to N_2 significantly lowered the catalytic activity (Entries 1 and 3). We previously reported that the photooxidation of alcohols proceeded through oxidative dehydrogenation to form the aldehyde, water, a vacancy in the lattice oxygen, and reduced Nb^{4+} sites, followed by recovery of Nb^{5+} and the lattice oxygen by O_2 (see Scheme S1 in the Supporting Information).[11] The lower catalytic activity in the absence of O_2 supports the idea that the reoxidation process by O_2 is necessary to function the catalytic cycle effectively. The reaction did not proceed at all in the absence of Nb_2O_5 under visible light (> 390 nm, Entry 4) or in the presence of Nb_2O_5 in the dark (Entry 9). These results suggest that the reaction is photocatalytic and neither any photoreaction nor thermal reaction is involved. When the wavelength of the incident light was expanded to > 350 nm, the selectivity towards the aldehyde was slightly decreased, owing to the formation of the carboxylic acid (Entries 1 and 5). In this case, very low conversion was obtained in the absence of Nb_2O_5. This indicated that the contribution from the photoreaction of the alcohol and/or the aldehyde themselves can be ignored and, hence, the carboxylic acid is formed through the photocatalytic reaction by using the bandgap excitation of Nb_2O_5. Selectivity towards the aldehyde significantly decreased because of the formation of the carboxylic acid under the irradiation of UV/Vis light of > 300 nm. Comparable conversion and selectivity were obtained in the absence of Nb_2O_5 in this wavelength region, indicating a large contribution of the photoreaction of the alcohol and/or the aldehyde. These results are consistent with the fact that the absorption edges of *p*-methoxybenzylalcohol and *p*-methoxybenzaldehyde are at approximately 320[13] and 350 nm,[14] respectively. Figure 2 shows the conversion-selectivity curves of the alcohol photooxidation in different wavelength regions of the incident light.

Table 1. Photooxidation of *p*-methoxybenzylalcohol over Nb_2O_5 with various conditions.[a]



Entry	Catalyst	λ [nm]	Time [h]	Conversion [%]	Selectivity [%][b]
1	+	> 390	6	48	> 99
2	+	> 390	16	99	> 99
3[c]	+	> 390	6	14	> 99
4	–	> 390	6	0	–
5	+	> 350	10	96	94 (6)
6	–	> 350	10	2	> 99
7	+	> 300	4	99	74 (24)
8	–	> 300	4	95	70 (11)
9	+	dark	6	0	–

[a] Reaction conditions: Nb_2O_5 catalyst (100 mg), *p*-methoxybenzylalcohol (1 mmol), $PhCF_3$ solvent (10 mL), oxygen pressure (1 atm.) [b] Selectivity towards *p*-methoxybenzoic acid is shown in parentheses. [c] Under 1 atm N_2.

In the presence of UV light (> 300 and > 350 nm), the selectivity gradually decreased with increasing conversion. Irradia-

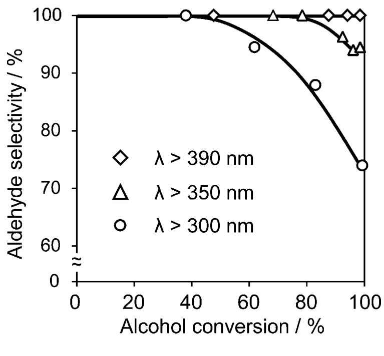
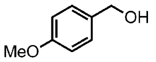
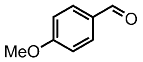
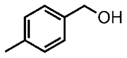
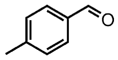
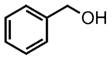
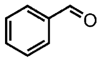
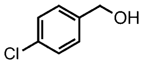
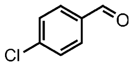
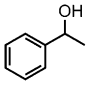
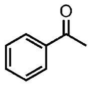
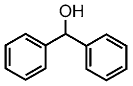
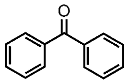
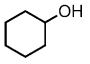
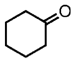


Figure 2. Conversion-selectivity curves for the photooxidation of *p*-methoxybenzylalcohol to the corresponding aldehyde in different wavelength regions of the incident light.

tion of the light >300 nm showed a steeper drop in selectivity than that at >350 nm. In contrast, >99% selectivity was maintained, even at 99% conversion, under the irradiation of visible light (>390 nm). Thus, the photooxidation of primary alcohols to aldehydes was successfully achieved by using Nb_2O_5, O_2, and visible light. We subsequently investigated the substrate scope of this photocatalytic system, as shown in Table 2. Benzylalcohol and its *p*-substituted derivatives (methoxy-, methyl-, and chloro-) were selectively converted into the corresponding aldehydes (Entries 1–4). Carboxylic acid was not formed at all in each case, even at high conversion levels. In the oxidation of *p*-methylbenzylalcohol, only a small amount of terephtalaldehyde was yielded as a byproduct. Other aromatic secondary alcohols, 1-phenylethanol and diphenylmethanol, were selectively converted to the corresponding ketones (Entries 5 and 6). Although the reaction rate was lower than those of aromatic alcohols, cyclohexanol was also oxidized to cyclohexanone with excellent selectivity (Entry 7). Thus, this photocatalytic system can be applied to the oxidation of various alcohols, including primary, secondary, aromatic, and aliphatic alcohols. As expected, the key points of this photocatalytic system involve the localized excitation from the donor level (alcoholic O 2p orbital), which enables the oxidation of adsorbed alcohols (alkoxide) into the corresponding aldehydes by using visible light, even though it is not absorbed by Nb_2O_5 itself. The lack of UV light excluded the involvement of bandgap excitation of Nb_2O_5 and photoreaction of an alcohol itself, both of which cause over oxidation of an aldehyde, forming the corresponding carboxylic acid. It should also be noted that the excited electrons and the trapped electrons at Nb^{5+} sites (namely, Nb^{4+} sites) do not trigger any oxidation reaction of organic molecules. We have already confirmed this in a previous study, as no oxidized product was formed during the reoxidation of Nb^{4+} to Nb^{5+} by using molecular oxygen.[15] Molecular oxygen is consumed in the reoxidation of Nb^{4+} and is used to recover the oxygen vacancies that are generated by oxidative dehydrogenation (see Scheme S1 in the Supporting Information). Recently, a similar photocatalytic system for alcohol oxidation with TiO_2 and visible light has also been reported.[16] Although the proposed photoexcitation mechanism differs slightly from that of our system, they are identical in that a strong interaction between an alcohol and a photocatalyst induces a visible-light-harvesting ability.

Table 2. Photooxidation of various alcohols over Nb_2O_5 under visible-light irradiation.[a]

Entry	Substrate	Product	Time [h]	Conversion [%]	Selectivity [%][b]
1			16	99	>99
2			16	96	97 (3)
3			16	80	>99
4			16	64	>99
5			16	59	>99
6			16	60	>99
7			16	5	>99
8			48	14	>99

[a] Reaction conditions: Nb_2O_5 catalyst (100 mg), alcohol (1 mmol), $PhCF_3$ solvent (10 mL), oxygen pressure (1 atm). [b] Figure in parenthesis is the selectivity towards terephtalaldehyde.

In summary, the aerobic photooxidation of primary alcohols into aldehydes selectively proceeded over Nb_2O_5 by using visible light. The obtained results not only indicate an attractive photocatalytic system, but also demonstrate the validity of our strategy for selective photocatalytic oxidation.

Keywords: alcohols · aldehydes · Nb_2O_5 · photooxidation · visible light

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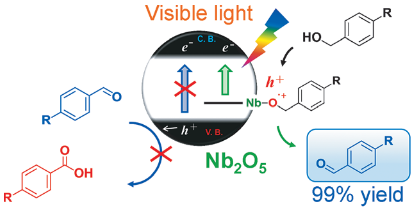

Primary alcohols are selectively converted into aldehydes by using a Nb_2O_5 photocatalyst under visible-light irradiation. A strong interaction between an alcohol and Nb_2O_5 generates a donor level within the forbidden band of Nb_2O_5, which provides the visible-light-harvesting ability. Overoxidation of aldehydes into carboxylic acids does not proceed under visible-light irradiation.