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Photocatalytic Oxidation of Alcohols over TiO_2 Covered with Nb_2O_5

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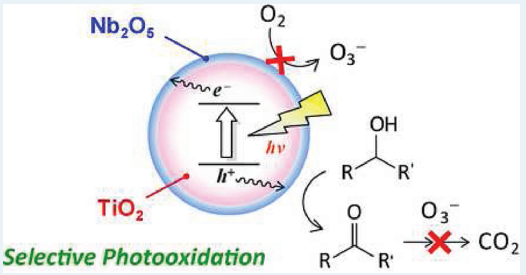
Supporting Information

ABSTRACT: A selectivity enhancement in alcohol photooxidation using TiO_2 covered with Nb_2O_5 is demonstrated. A series of TiO_2 covered with Nb_2O_5 catalysts (Nb_2O_5/TiO_2, loading of Nb_2O_5; 0−5 mol %) were prepared and characterized. XPS studies suggest that the TiO_2 surface was completely covered with Nb_2O_5 at a 3.5 mol % loading. UV−vis spectra of TiO_2 and the Nb_2O_5/TiO_2 series revealed that the band gap energy of the catalyst was not changed upon addition of Nb_2O_5. The amounts of photogenerated oxygen anion radical species (O_2^- and O_3^-) over the catalyst, as estimated by ESR, drastically decreased with increased loadings of Nb_2O_5. The O_3^- anion, in particular, which can be formed on anatase TiO_2, completely disappeared at Nb_2O_5 loadings over 4 mol %. In the oxidations of several alcohols (1-pentanol, 2-pentanol, 3-pentanol, and cyclohexanol), the Nb_2O_5/TiO_2 catalysts exhibited higher selectivities than TiO_2 with comparable conversion levels. Furthermore, the Nb_2O_5/TiO_2 system gave a higher photocatalytic activity compared with Nb_2O_5 without lowering the selectivity.



KEYWORDS: *surface coverage, monolayer, titanium oxide, niobium oxide, alcohol photooxidation*

INTRODUCTION

Heterogeneous photocatalysis has a potential application in the aerobic oxidation of organic molecules.[1−3] Numerous semiconductor-type metal oxides have been tested as photocatalysts for oxidation, but it is generally accepted that anatase TiO_2 is the most reliable material due to its low cost, high photostability, and photocatalytic activity. Recently, much effort has been devoted to the application of TiO_2 to the selective catalytic oxidation of alkanes[4−7] and alcohols;[8−15] however, undesired overoxidation to carbon dioxide (CO_2) is essentially associated with the photocatalytic oxidation over TiO_2 due to the presence of highly oxidizing radical species: positive holes trapped by surface lattice oxygen (O^-),[16,17] ozonide ion (O_3^-),[18,19] or the hydroxyl radical ($HO\cdot$).[2] It is generally accepted that O_3^- is formed upon the combination of O^- and O_2[18−20] and that $HO\cdot$ is released via the oxidation of a surface hydroxyl group by a hole.[2,21] Tsukamoto et al. reported that TiO_2 partially coated with WO_3 showed higher activity and selectivity in the photooxidation of benzylic alcohols to aldehydes than TiO_2 under diluted conditions (5 mg of catalyst, 0.1 mmol of alcohol, and 5 mL of water as a solvent).[22] They interpret that the phenomena that TiO_2 surface of the catalyst, which is active for oxidation, is partially coated with WO_3 layer (WO_3 loading: 7.6 wt %), which leads to a decrease in the amount of aldehyde adsorbed on the TiO_2 surface. It appeared that the area of TiO_2 surface was decreased by WO_3 addition. However, not only the selectivity to aldehyde but also the rate of alcohol conversion increased. Therefore, it seems that the WO_3 layer has another role in addition to the adsorption site of photogenerated aldehyde.

We reported that the selective photooxidation of alcohols proceeded over niobium oxide (Nb_2O_5) and showed a higher selectivity than TiO_2 with a comparable conversion level.[23] ESR studies suggested that this high selectivity was due to the absence of O_3^- over Nb_2O_5, in contrast to TiO_2 under photo irradiation;[24] however, the photocatalytic activity of Nb_2O_5 in the oxidation of alcohols was much lower than that of TiO_2. To develop an effective photocatalyst that exhibits both high activity and selectivity in the aerobic oxidation of alcohols, there are two primary strategies: improve the photocatalytic activity of Nb_2O_5 or enhance the selectivity of TiO_2. In the first strategy, we have already achieved a remarkable increase in photocatalytic activity by addition of Cu to Nb_2O_5.[25] In the oxidation of alcohols over Cu/Nb_2O_5, the Cu(I) site operates as a desorption site and successfully promotes the desorption of the produced carbonyl compound, which is the rate-determining step.[26] In the latter, attention should be focused on how the formation of the highly oxidizing species above-mentioned is inhibited. In this context, a promising approach is to cover the surface of TiO_2 with Nb_2O_5 ,which inhibits the production of highly oxidizing O_3^- (Scheme 1).

In this study, we have prepared a series of TiO_2 covered with Nb_2O_5 photocatalysts and their photocatalytic activities and selectivities have been compared with those of bare TiO_2 or Nb_2O_5 in the oxidation of alcohols. The correlation between the amount of photogenerated oxygen anion radicals and selectivity has also been investigated. Here in, we demonstrate that it is effective for selective oxidation using TiO_2-based photocatalysts to inhibit the formation of O_3^- by surface coverage of TiO_2.

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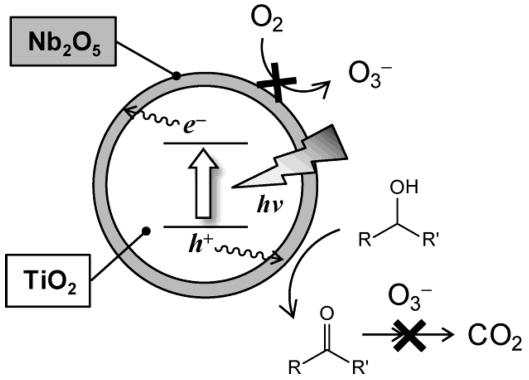
Scheme 1. Strategy for the Selective Photocatalytic Oxidation of Alcohols over Nb_2O_5/TiO_2[a]



[a]The inhibition of O_3^- generation by surface coverage of TiO_2 with Nb_2O_5 is shown.

EXPERIMENTAL SECTION

Catalyst Preparation. Ammonium niobium oxalate ($NH_4[NbO(C_2O_4)_2(H_2O)]\cdot nH_2O$), as a precursor of niobium oxide, and niobium oxide hydrate ($Nb_2O_5\cdot nH_2O$, HY-340) were kindly supplied by CBMM (Araxa, Brazil). The TiO_2 sample used in this study, JRC-TIO-4 (equivalent to Degussa. P-25; rutile/anatase = 3/7; BET surface area = 49 $m^2\cdot g^{-1}$) was supplied by the Japan Catalysis Society. After the hydration of TiO_2 in distilled water for 2 h at 353 K and evaporation at 368 K, the sample was dried at 353 K overnight. The TiO_2 catalyst was then calcined in dry air at 773 K for 5 h. A series of TiO_2 supported niobium oxide catalysts (n mol % Nb_2O_5/TiO_2; n = 1−5) were prepared by impregnation of the TiO_2 sample with aqueous solutions of ammonium niobium oxalate followed by calcination at 773 K for 5 h. Nb_2O_5 catalyst (BET surface area = 48 $m^2\cdot g^{-1}$)[23] was prepared by calcination of niobium oxide hydrate in a dry air flow at 773 K for 5 h. All catalysts were ground into powders under a 100 mesh (0.15 mm) after calcination.

Characterization. A Rigaku MultiFlex DR Powder X-ray diffractometer (XRD) was used for the identification of compounds formed on the catalyst samples. Specific surface areas were evaluated using the BET method using liquid nitrogen with a BEL Japan BELSORP28 28A. UV−vis diffuse reflectance spectra (1 nm resolution) were obtained with a JASCO UV570 spectrometer. X-ray photoelectron spectra (XPS) were acquired using an ULVAC PHI 5500MT. XPS samples were mounted on an indium foil, and the spectra were measured using Mg Kα radiation (15 kV, 400 W) in a chamber with the base pressure of ~10^{-9} Torr. The takeoff angle was set at 45°. Binding energies were referenced to the O 1s level at 530.2 eV.

ESR Measurement of Oxygen Anion Radicals. ESR measurements were carried out using an X-band ESR spectrometer (JEOL JES-SRE2X) with an in situ quartz cell. Prior to ESR measurement, the sample was pretreated with 6.7 kPa O_2 at 673 K for 1 h, followed by evacuation for 0.5 h at 673 K. After pretreatment, the sample was exposed to 0.5 kPa O_2 at room temperature. The sample was then cooled to 123 K and irradiated. ESR spectra were recorded before and after photoirradiation at 123 K. The g values and the amounts of yielded radical species were determined using a certain amount of Mn/MgO marker. The radical amounts of the Mn/MgO marker were determined using 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL; radical density 97%, purchased from Wako). A 500 W ultrahigh-pressure mercury lamp was used as a light source.

Reaction Conditions. The photocatalytic oxidations of alcohols were carried out in a quasi-flowing batch system[25] (see Supporting Information, Figure S1) under atmospheric oxygen. The catalyst (100 mg), alcohol (10 mL), and a stirrer bar were introduced to a Pyrex glass reactor. No solvent was used. The substrate was used without further purification. The suspension was vigorously stirred at room temperature and irradiated from the flat bottom of the reactor via reflection using a cold mirror with a 500 W ultrahigh-pressure Hg lamp (USHIO Denki Co.). Oxygen was flowed into the reactor at 2 $cm^3\cdot min^{-1}$. Organic products were analyzed by FID-GC (Shimadzu GC-14B) and GC-MS (Shimadzu GC-MS QP5050). At the down stream of the flow reactor, a saturated barium hydroxide solution ($Ba(OH)_2$) was set up to determine the quantities of carbon dioxide (CO_2) formed as barium carbonate ($BaCO_3$). The partial oxidation product selectivities are defined as yields (mmol) of aldehyde and acid (partial oxidation products) per yield (mmol) of aldehyde, acid and $1/n$ CO_2 (n = the number of carbon atoms of the substrate).

RESULTS AND DISCUSSION

Characterization of Catalysts. The valences of niobium and titanium cations in a few atomic layers of the Nb_2O_5/TiO_2 catalyst surface were evaluated using XPS. The binding energies of the Nb 3d and Ti 2p peaks of Nb_2O_5/TiO_2 did not change, regardless of Nb_2O_5 loading (Figure S2 of the Supporting Information). These Nb 3d (207.1 eV for $3d_{5/2}$ and 209.8 eV for $3d_{3/2}$) and Ti 2p (464.5 eV for $2p_{3/2}$ and 458.8 eV for $2p_{1/2}$) peaks can be assigned to Nb^{5+} and Ti^{4+}, respectively. The Nb/Ti ratios in a few atomic layers of the Nb_2O_5/TiO_2 catalyst surface were estimated from the areas of Nb 3d and Ti 2p XPS, as shown in Figure 1. The Nb/Ti ratio increases linearly with

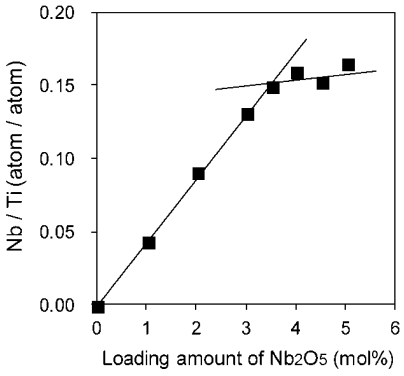


Figure 1. Changes in surface Nb/Ti ratio with Nb_2O_5 loading.

increasing Nb_2O_5 loading up to 3.5 mol % (equivalent to 10 wt %). It then becomes more gradual. The linear relationship indicates the formation of a two-dimensional niobium oxide overlayer, and the change in the slope can be attributed to the transition from a two-dimensional overlayer to three-dimensional particles (monolayer coverage) at loadings over 3.5 mol % Nb_2O_5.[27]

The XRD patterns of a series of Nb_2O_5/TiO_2 catalysts were compared with those of TiO_2 and Nb_2O_5, as shown in Figure 2. The patterns for 1−4 mol % Nb_2O_5/TiO_2 samples indicate no changes in the crystallinity of the TiO_2 support (anatase and

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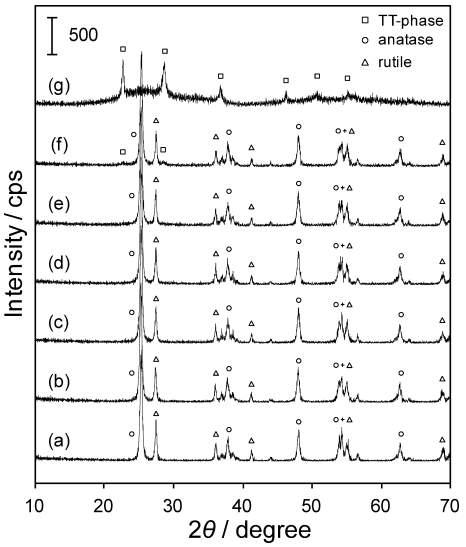

Figure 2. XRD patterns of (a) TiO_2; (b) 1, (c) 2, (d) 3, (e) 4, and (f) 5 mol % Nb_2O_5/TiO_2; and (g) Nb_2O_5.

rutile) and no formation of a niobium oxide crystallite. On the other hand, the 5 mol % Nb_2O_5/TiO_2 exhibits a small feature assignable to TT-Nb_2O_5,[28−31] which is associated with TiO_2. Similar diffraction patterns have also been reported for 7.7[32] or 11[33] mol % Nb_2O_5/TiO_2 samples. The formation of a niobium oxide crystallite at loadings over 3.5 mol % is consistent with the results from the XPS study. UV−vis spectra of the 1−5 mol % Nb_2O_5/TiO_2 catalysts were also identical to that of TiO_2 (Supporting Information Figure S3), whose band gap energy was estimated as 3.10 eV. The Nb_2O_5 catalyst possesses spectral features similar to that of TiO_2, and the band gap energy was estimated as 3.16 eV (Supporting Information Figure S3). Thus, the surface coverage of TiO_2 with Nb_2O_5 does not influence the crystallinity of the TiO_2 support and does not change the optical properties of the catalysts. The BET surface area measurements revealed that the surface area of TiO_2 (49 $m^2 \cdot g^{-1}$) was maintained after the addition of Nb_2O_5 (Supporting Information Figure S4).

ESR Measurements of Photogenerated Oxygen Anion Radicals. We characterized the photogenerated oxygen anion radical species over TiO_2, Nb_2O_5/TiO_2, and Nb_2O_5 using ESR and estimated the amounts of the radical species. Figure 3

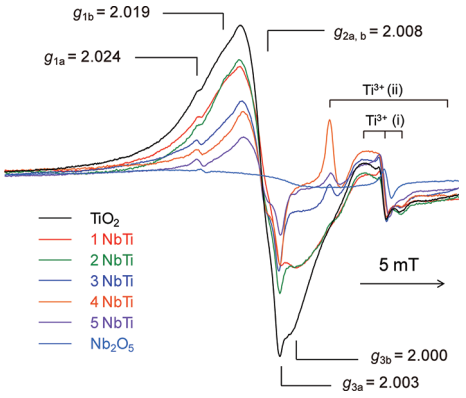

Figure 3. ESR spectra of the photogenerated oxygen anion radical at 77 K over TiO_2, *n* mol % Nb_2O_5/TiO_2 (abbreviated as *n*NbTi; *n* = 1, 3, 5), and Nb_2O_5.

shows the ESR spectra obtained when the catalysts were irradiated in the presence of oxygen at 123 K. An intense signal consisting of two sets of rhombic *g* values were observed over TiO_2, which can be assigned to superoxide (O_2^-: g_1 = 2.024, g_2 = 2.009, g_3 = 2.003)[34−36] and ozonide (O_3^-: g_1 = 2.019, g_2 = 2.006, g_3 = 2.000).[35−38] Such radical species over TiO_2 are well-known and have been widely characterized. Generally, it is proposed that the O_2^- is generated via the reduction of adsorbed O_2 by excited electrons. The O_3^- is formed from the combination of a positive hole captured by surface lattice oxygen (equivalent to O^-) and O_2.[20,35,39,40] In contrast, only a small broad signal was observed over Nb_2O_5. In this case, using ^{17}O-enriched O_2 (20%) instead of $^{16}O_2$, a signal appeared with hyperfine splitting, as derived from the ^{17}O nuclei (I = 5/2) (Supporting Information Figure S5). This hyperfine structure indicates the generation of $^{16}O^{17}O^-$ and suggests that the two oxygen nuclei are equivalent. The equivalent hyperfine interactions are also consistent with the O_2^- ion being adsorbed in a side-on fashion onto the Nb_2O_5 surface, with its internuclear axis parallel to the plane of the surface. This type of adsorption is commonly observed with other metal oxides.[20] Eleven lines corresponding to the two ^{17}O nuclei ($^{17}O^{17}O^-$, I = 5) were expected, but apparently not observed, which is likely due to an inadequate enrichment of ^{17}O (20%).

The intensities of the ESR signals for the oxygen anion radicals were dramatically decreased with increasing of Nb_2O_5 loading. Although the signals assigned to O_2^- remained at a 5 mol % loading, the signal assigned to O_3^- completely disappeared at loadings over 4 mol %. This result strongly indicates that the TiO_2 surface, which can produce O_3^-, is completely covered at loadings over 4 mol %. It is also consistent with a monolayer coverage at 3.5 mol % loading, as estimated from the XPS study. The amounts of photogenerated oxygen anion radical species are shown in Figure 4. The

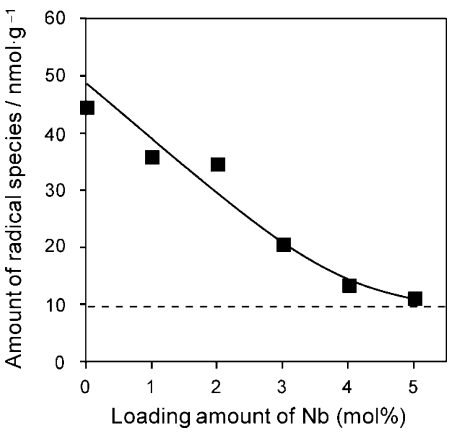

Figure 4. Changes in the amount of photogenerated oxygen anion radical species (O_2^- + O_3^-) over Nb_2O_5/TiO_2 catalyst with Nb_2O_5 loading. The dotted line shows the radical amount over Nb_2O_5.

amount of the radical species drastically decreases on going from 0 to 4 mol % Nb_2O_5 loading. This change becomes gradual at loadings over 4 mol %. Thus, these results demonstrate that the surface coverage of TiO_2 with Nb_2O_5 effectively inhibits the formation of oxygen anion radicals. In particular, the generation of O_3^- was completely inhibited by full coverage (Scheme 2). The *g* values of the ESR signal assigned to O_2^-, as generated on 5 mol % Nb_2O_5/TiO_2, are different from those on TT-Nb_2O_5. This may be due to the

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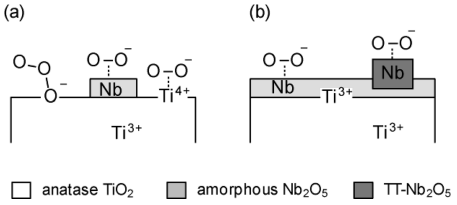
Scheme 2. Plausible Surface Species on the Nb_2O_5/TiO_2: (a) below 3 mol % Nb_2O_5 Loading and (b) over the Monolayer



differences in crystallinity of Nb_2O_5 (amorphous or TT-phase). The ESR spectrum of the oxygen anion radicals formed on 5 mol % Nb_2O_5/TiO_2 has a shoulder feature in the region of g = 2.003−2.008. This is in good agreement with the peak features of O_2^-, formed on TT-Nb_2O_5 in the same region (Supporting Information Figure S5), which implies the formation of O_2^- on TT-Nb_2O_5 (Scheme 2).

In addition to the signals of the oxygen anion radicals, small signals were also observed in the region of $g < 2.000$. These can be assigned to excited electrons trapped by the Ti^{4+} sites (equivalent to Ti^{3+}) and are composed of two distinct signals (Ti^{3+} (i) and (ii)). The g values of Ti^{3+} (i) (g_1 = 1.982, g_2 = 1.977, g_3 = 1.971) are similar to those for bulk and surface Ti^{3+} in TiO_2.[41] The g values and the signal intensity do not depend on the loading amount of Nb_2O_5. These suggest that the Ti^{3+} (i) corresponds to the bulk Ti^{3+} site. On the other hand, the signals assigned to Ti^{3+} (ii) are only observed with a large surface coverage of TiO_2 (>3 mol %). The g values of Ti^{3+} (ii) ($g_\perp$ = 1.990, $g_{||}$ = 1.962) are almost identical to those obtained from Nb-doped anatase TiO_2 and are attributed to the interstitial Ti^{3+} ion.[42,43] On this basis, the Ti^{3+} (ii) is assignable to the interfacial Ti^{3+} sites adjacent to loaded Nb_2O_5 (Scheme 2).

Photocatalytic Activity and Selectivity. The photocatalytic activities and selectivities of the TiO_2, Nb_2O_5/TiO_2, and Nb_2O_5 catalysts were evaluated using the photooxidation of 1-pentanol, as shown in Figure 5. Although the photocatalytic activity gradually decreases as the loading of Nb_2O_5 is increased, 5 mol % Nb_2O_5/TiO_2, which seems to be fully covered with Nb_2O_5, still exhibits a higher activity than Nb_2O_5. If the excited electrons or positive holes generated in the inner TiO_2 core cannot be transferred to the surface Nb_2O_5 thin layer, the photocatalytic activity of the fully covered Nb_2O_5/TiO_2 catalyst (>4 mol % loading) should be lower than that of bare Nb_2O_5. Therefore, the photogenerated charge carriers due to band gap excitation of the inner TiO_2 core can be transferred to the catalyst surface and used for the alcohol oxidation.

The selectivity to partial oxidation products became higher on going from 1 to 5 mol % loading and reached 97%, which is as high as that obtained with Nb_2O_5 (Figure 5a). The higher selectivities of the Nb_2O_5/TiO_2 catalysts, as compared with the TiO_2, are maintained at the same conversion level (Figure 5b). Thus, the surface coverage of TiO_2 with Nb_2O_5 effectively enhances the selectivity of the photooxidation of 1-pentanol. The selectivity at comparable conversion levels increased with increasing Nb_2O_5 loading up to 3 mol %.

As mentioned above, the ESR study revealed that coverage of the TiO_2 surface with Nb_2O_5 inhibits the generation of O_3^-, which is highly active toward the complete oxidation of organic molecules. In fact, O_3^- is known to be active even at room temperature, whereas O_2^- is stable up to ca. 423 K. On this basis, the change in selectivity on going from 0 to 3 mol %

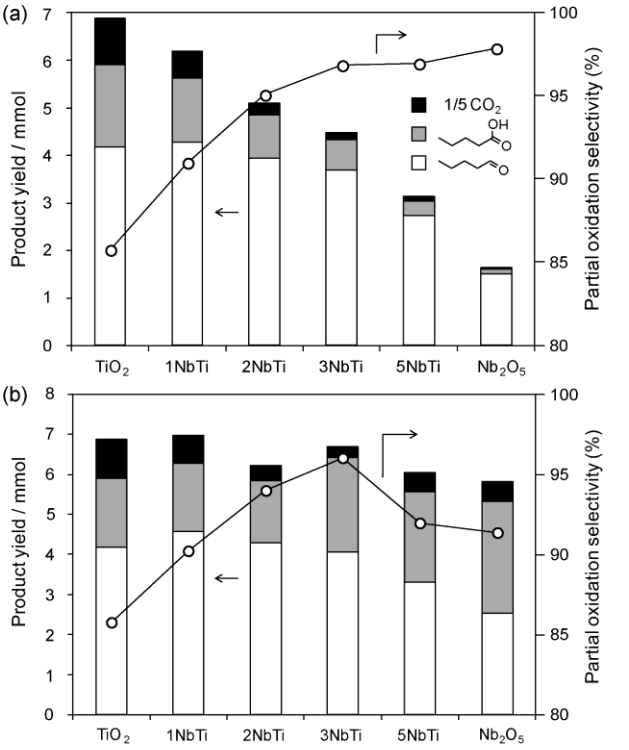


Figure 5. Product yields in the photooxidation of 1-pentanol over TiO_2, n mol % Nb_2O_5/TiO_2 (abbreviated as nNbTi; n = 1, 2, 3, and 5) and Nb_2O_5; (a) after 5 h of photo irradiation, (b) at a comparable conversion level (TiO_2; 5 h, 1NbTi; 5.5 h, 2NbTi; 6 h, 3NbTi; 7.5 h, 5NbTi; 13 h and Nb_2O_5; 20 h).

Nb_2O_5 loading agrees with the results from the ESR study. However, 5 mol % Nb_2O_5/TiO_2 and Nb_2O_5 showed lower selectivities compared with 3 mol %. In this case, higher yields of pentanoic acid are obtained than the lower loading homologues. This indicates that overoxidation of the products to CO_2 takes place more severely for 5 mol % Nb_2O_5/TiO_2 and Nb_2O_5 due to the much longer reaction times. Figure 6 shows

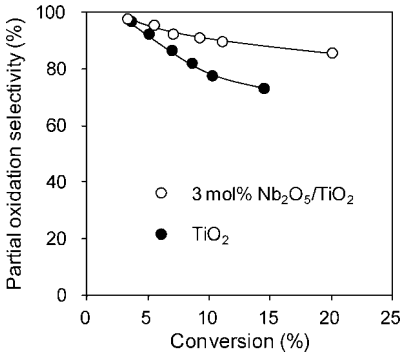


Figure 6. Selectivity-conversion plots for the photooxidation of 1-pentanol over 3 mol % Nb_2O_5/TiO_2 and TiO_2.

the relationship between selectivity and conversion in the photooxidation of 1-pentanol over 3 mol % Nb_2O_5/TiO_2 and TiO_2. At the higher conversion level, 3 mol % Nb_2O_5/TiO_2 catalyst exhibited a much higher selectivity than TiO_2. The 3 mol % Nb_2O_5/TiO_2 catalyst maintained more than 85% selectivity, even at 20% conversion. However, the selectivity fell below 75% at 15% conversion when TiO_2 was used.

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We went on to apply 3 mol % Nb_2O_5/TiO_2 to the oxidation of various alcohols. The activities and selectivities were compared with those of TiO_2 and Nb_2O_5 (Supporting Information Figure S6). The oxidation of several secondary alcohols (2-pentanol, 3-pentanol, cyclohexanol) gave the corresponding ketones and certain amounts of CO_2. In each case, the 3 mol % Nb_2O_5/TiO_2 catalyst showed not only a much higher activity than Nb_2O_5 without lowering selectivity, but also a higher selectivity than TiO_2 at a comparable conversion level. Thus, the surface coverage of TiO_2 with Nb_2O_5 enhanced the selective partial oxidation of various alcohols, including primary and secondary alcohols.

CONCLUSIONS

In this study, we prepared a series of TiO_2 supported Nb_2O_5 catalysts (Nb_2O_5/TiO_2, with loadings of Nb_2O_5 between 0−5 mol %) for the selective photooxidation of alcohols. XPS studies suggested that the TiO_2 surface was completely covered with Nb_2O_5 at loadings over 3.5 mol %. UV−vis spectra of TiO_2 and a series of Nb_2O_5/TiO_2 samples revealed that the absorption band of the catalyst remained unchanged by the addition of Nb_2O_5; however, the amounts of photogenerated O_2^- and O_3^- over the catalyst were estimated by ESR to be drastically decreased with increased loadings of Nb_2O_5. In particular, O_3^-, which can be formed on anatase TiO_2, completely disappeared at loadings over 4 mol %. We also investigated the photocatalytic activities and selectivities of these catalysts in the oxidation of 1-pentanol. Although the photocatalytic activity gradually decreased with increasing of Nb_2O_5 loading, the selectivity was enhanced. At a comparable conversion level, the maximum selectivity was obtained with a 3 mol % Nb_2O_5 loading. Similarly, 3 mol % Nb_2O_5/TiO_2 exhibited higher selectivities than TiO_2 in the oxidation of secondary alcohols (2-pentanol, 3-pentanal, and cyclohexanol). Thus, the surface coverage of TiO_2 with Nb_2O_5 effectively enhanced the selectivity to partial oxidation product(s) in alcohol photooxidation, due to inhibition of O_3^- formation. Furthermore, the present study proves the strategy to inhibit the formation of active oxygen species effective and provides a new promising basis for selective oxidation using TiO_2-based photocatalysts.

ASSOCIATED CONTENT

Supporting Information

Setup of reactor, XPS, UV−vis spectra, surface areas of catalysts, ESR spectra, and substrate scope. This material is available free of charge via the Internet at http://pubs.acs.org.

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