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Unique photo-activation mechanism by “in situ doping” for photo-assisted selective NO reduction with ammonia over TiO$_2$ and photooxidation of alcohols over Nb$_2$O$_5$

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This paper reviews the recent development of the photocatalytic emission control reaction and photooxidation with molecular oxygen, specifically focusing on efforts based on the revealing the reaction mechanism by the authors’ group. TiO$_2$ acts as an effective catalyst for the photo-assisted selective catalytic reduction of NO with NH$_3$ in the presence of O$_2$ (photo-SCR). Photooxidation of alcohols to carbonyl compounds proceeds selectively over Nb$_2$O$_5$ without organic solvents. Usually, both TiO$_2$ and Nb$_2$O$_5$ work only in the ultraviolet (UV) region because of the limit of their bandgap energies. However, both photo-SCR over TiO$_2$ and photooxidation of alcohols over Nb$_2$O$_5$ proceed even under visible light irradiation up to ca. 450 nm. This indicates that these two reactions take place by the different photo-activation mechanism from the classical electron transfer mechanism in semiconductor photocatalysis, that is, the formation of an excited electron in the conduction band and the positive hole in the valence band. A mechanistic study using UV-Vis, ESR, FT/IR, kinetic study, and DFT calculations revealed the reaction mechanisms of photo-SCR and photooxidation of alcohols, and that the surface complex consisting of adsorbed molecule and catalyst plays an important role in the photo-activation step.

The surface complex is converted to the photo-activated species even under visible light irradiation, because the direct electron transition from a donor level derived from adsorbed molecule to the conduction band of photocatalyst takes place and photo-generated hole is trapped on adsorbed molecule to form the photo-activated radical species. The effective wavelength is shifted to a longer wavelength by the formation of donor level derived from adsorbed molecule during a chemical reaction (called here “in situ doping”). This unique photo-activation mechanism by “in situ doping” gives us attractive ways for the removing the limit of bandgap energy, and the utilization of visible light.

1. Introduction

As shown in Scheme 1, photocatalytic reactions on a semiconductor powder involves several steps. Photocatalysis is generally explained in terms of band theory (the classical electron transfer mechanism) accompanied by the interaction of reactants with the photo-generated electrons and holes, and is potentially available to make the catalytic reactions proceeding at low temperature. The band structure of the photocatalysts determines the utilizable light energy, oxidizability, and reducing ability. It has been considered that suppressing recombination between photo-generated electrons and holes in a photocatalyst is important to achieving the reaction, since the lifetime of the charge separation contributes to the photocatalytic activity.

Therefore, a number of studies are related to the control of band structure and charge separation. On the other hand, little information about the adsorbed species and the intermediates in photocatalytic reactions is available. Photocatalytic reactions take place on the surface of the photocatalysts as well as the ordinary catalysts. The difference between the photocatalysts and the ordinary catalysts is just the driving force to activate the adsorbed
reactants; the photocatalysts use the photo-energy and the ordinary catalysts use the thermal energy. Therefore, the kinetic interpretation and the knowledge of surface structure, surface property, and surface species during the photo-reaction are required to understand the photocatalysis; generally a catalytic reaction consists of several elementary steps and one or two of the elementary steps involves absorption of light in the case of a photocatalytic reaction. Hence, there is the same thermodynamic restriction in the photocatalysis with the ordinary catalysis. Evidently, it is necessary to consider the photo-activation mechanism in detail. The clarification of the reaction mechanism provides the beneficial information on the further improvement of the photocatalysis and a new insight of photocatalytic chemistry.

This article summarizes our recent work on the photo-activation mechanisms of NH\(_3\) over TiO\(_2\) in photo-SCR, and alcohols over Nb\(_2\)O\(_5\) in the photooxidation with molecular oxygen. We show a detailed investigation of reaction mechanisms of photo-SCR over TiO\(_2\) and selective photooxidation of alcohols over Nb\(_2\)O\(_5\) using in situ characterization, kinetic study and DFT calculations. A redshift of effective wavelength due to the direct electron transition from the donor level derived from adsorbed molecule to the conduction band ("in situ doping") is demonstrated.

2. Photo-assisted selective reduction of NO with NH\(_3\) over TiO\(_2\) based catalysts

2.1 Low-temperature NH\(_3\)-SCR systems

The growth of the global economy involved the environmental problems such as solid, air and water pollutions. These pollutions cause serious damage to human and nature. In order to solve these problems, many efforts are being made concerning the development of the environmental technology.

NO\(_x\) is one of the environmental pollutants and causes acid rain and photochemical smog. Therefore, it is desirable to remove NO\(_x\) (de-NO\(_x\)) in the stationary emission source and the mobile emission source. In the stationary emission source such as a thermal power station, an industrial boiler and a waste incinerator, NO\(_x\) is conventionally removed from the exhaust gas by the selective catalytic reduction system with NH\(_3\) as a reductant (NH\(_3\)-SCR) in the presence of the excess O\(_2\) over V\(_2\)O\(_5\)-WO\(_3\) (or V\(_2\)O\(_5\)-MoO\(_3\))/TiO\(_2\) catalyst.\(^{1,4}\) This technology was invented by three Japanese corporations (Hitachi Ltd., Babcock-Hitachi K. K., Mitsubishi Petrochemical Corp.).\(^{5}\) The reaction stoichiometry in the typical NH\(_3\)-SCR is shown as follows;

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1)
\]

N\(_2\) is formed by the reaction of NO with NH\(_3\),\(^{5,11}\) N\(_2\)O is a by-product. This system shows high NO conversion (99%), high N\(_2\) selectivity (> 90%) and resistance for H\(_2\)O and SO\(_x\), although the catalyst requires high operating temperature (573–673 K).\(^{12}\) Since the exhaust gas contains various pollutants and materials such as SO\(_x\), halogen compounds, particulate matter (PM) and fly ash in addition to NO\(_x\), the NH\(_3\)-SCR system is used together with de-SO\(_x\), de-halogen and dust collection systems. Thus, the NH\(_3\)-SCR system is often located downstream of the de-SO\(_x\), de-halogen and dust collection systems in order to inhibit deactivation of V\(_2\)O\(_5\)-WO\(_3\) (or V\(_2\)O\(_5\)-MoO\(_3\))/TiO\(_2\) catalyst. In this case, the inlet temperature of the exhaust gas in the NH\(_3\)-SCR system falls below 453 K. Consequently, it is necessary to re-heat the catalysis bed and the gas up to the operating temperature of the catalyst. Therefore, it is desired to develop a new de-NOX system working at low temperature (< 453 K). Since the 1990s, the low-temperature NH\(_3\)-SCR has been investigated to develop the new NH\(_3\)-SCR system capable of operating under 453 K. The following is a request for the low-temperature NH\(_3\)-SCR system: (1) NO\(_x\) conversion must be high (more than 90%), (2) N\(_2\) selectivity must be high (more than 90%), (3) catalysts must have high durability to H\(_2\)O, and (4) NH\(_3\)-SCR system must be operated in the presence of an excess O\(_2\). Since H\(_2\)O vapor gets mixed in with the exhaust gas in the de-SO\(_x\) and the de-halogen processes, the catalysts must have high durability to H\(_2\)O. The low-temperature NH\(_3\) SCR systems reported are listed in Table 1.\(^{13-19}\) The first report of the NH\(_3\)-SCR is MnO\(_2\)-Al\(_2\)O\(_3\) catalyst reported by Singoredo et al.\(^{14}\) MnO\(_2\)-Al\(_2\)O\(_3\) catalyst had poor durability to H\(_2\)O and the activity decreased with the course of the reaction time.

**Table 1** Low-temperature SCR reaction systems

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NO (ppm)</th>
<th>NH(_3) (ppm)</th>
<th>O(_2) (ppm)</th>
<th>H(_2)O (%)</th>
<th>T (K)</th>
<th>SV (h(^{-1}))</th>
<th>X(_{\text{NO}}) (%)</th>
<th>S(_{\text{N}_2}) (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO(_2)-Al(_2)O(_3)</td>
<td>550</td>
<td>550</td>
<td>2</td>
<td>0</td>
<td>435</td>
<td>31,000</td>
<td>98</td>
<td>92</td>
<td>11</td>
</tr>
<tr>
<td>MnO(_2)-carbonized silica-alumina</td>
<td>800</td>
<td>800</td>
<td>3</td>
<td>0</td>
<td>413</td>
<td>12,000</td>
<td>94</td>
<td>91</td>
<td>13</td>
</tr>
<tr>
<td>MnO(_2)-NaY</td>
<td>1000</td>
<td>1000</td>
<td>10</td>
<td>7</td>
<td>443</td>
<td>48,000</td>
<td>88</td>
<td>93</td>
<td>17</td>
</tr>
<tr>
<td>MnO(_2)-TiO(_2)</td>
<td>2000</td>
<td>2000</td>
<td>2</td>
<td>0</td>
<td>393</td>
<td>8,000</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>MnO(_2)-TiO(_2)</td>
<td>400</td>
<td>400</td>
<td>11</td>
<td>11</td>
<td>448</td>
<td>50,000</td>
<td>98</td>
<td>97</td>
<td>19</td>
</tr>
<tr>
<td>Fe-Mn oxide</td>
<td>1000</td>
<td>1000</td>
<td>2</td>
<td>0</td>
<td>393</td>
<td>15,000</td>
<td>100</td>
<td>100</td>
<td>16</td>
</tr>
<tr>
<td>Fe-Mn oxide</td>
<td>1000</td>
<td>1000</td>
<td>2</td>
<td>2.5</td>
<td>413</td>
<td>15,000</td>
<td>98</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>MnO(_2)-CoO</td>
<td>1000</td>
<td>1000</td>
<td>2</td>
<td>0</td>
<td>393</td>
<td>42,000</td>
<td>99</td>
<td>100</td>
<td>15</td>
</tr>
<tr>
<td>MnO(_2)-CoO</td>
<td>1000</td>
<td>1000</td>
<td>2</td>
<td>19</td>
<td>393</td>
<td>42,000</td>
<td>95</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>V(_2)O(_5)-sulphated carbon</td>
<td>500</td>
<td>600</td>
<td>3</td>
<td>0</td>
<td>453</td>
<td>34,000</td>
<td>92</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

\(^{*}\) T: Reaction temperature. SV: Space velocity. X\(_{\text{NO}}\): NO conversion. S\(_{\text{N}_2}\): N\(_2\) selectivity
Subsequently, several Mn-containing catalysts, which show the high activity with the durability to H2O at a low-temperature, are reported. Among the Mn-containing catalysts reported, MnO2-CeO2 shows the highest activity (95% NO conversion and 100% N2 selectivity in the presence of 19% H2O). The reaction was carried out in a closed system and the activity was very low. On the contrary, we found that TiO2 and metal oxide promoted TiO2 are effective for the photo-SCR with NH3 in the presence of O2.

2.2 Photo-SCR with NH3 over TiO2 Photocatalysts

Over the past decades, the most attentions of the photocatalysis has been gathered to the water photolysis and the removal of harmful compounds over photocatalysts responding to visible light. In contrast, although photocatalysts have the advantage that the re-heating of catalyst bed is unnecessary because of their possibility of application at low temperatures, the reports of the NH3-SCR reaction over photocatalysts (photo-SCR) were limited. Cant et al. reported that NO reduction by NH3 to form N2 proceeds over TiO2 under photo-irradiation. The reaction was carried out in a closed system and the activity was very low. On the contrary, we found that TiO2 and metal oxide promoted TiO2 are effective for the photo-SCR with NH3 in the presence of O2 proceeds at room temperature.

Table 2 shows the catalytic activity and physicochemical property of photo-SCR with NH3 over various TiO2 photocatalysts (JRC-TIO-1-13 supplied from Catalysis Society of Japan). JRC-TIO-11, a mixture of rutile and anatase phases, exhibited the highest activity among all TiO2 tested. JRC-TIO-8 and JRC-TIO-3 were the most active catalysts consisting of anatase or rutile single phases. There is poor correlation between the activity and crystal phase, crystallite size, and specific surface area. This indicates that these properties are not the important factors to determine the activity of photo-SCR.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Sa (m2/g)</th>
<th>Phase</th>
<th>D0 (Å)</th>
<th>NO conv. (%)</th>
<th>N2 sel. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JRC-TIO-1</td>
<td>71.1</td>
<td>A</td>
<td>187</td>
<td>36</td>
<td>100</td>
</tr>
<tr>
<td>JRC-TIO-2</td>
<td>15.6</td>
<td>A</td>
<td>535</td>
<td>14.5</td>
<td>100</td>
</tr>
<tr>
<td>JRC-TIO-3</td>
<td>45.6</td>
<td>R</td>
<td>219</td>
<td>53</td>
<td>100</td>
</tr>
<tr>
<td>JRC-TIO-4</td>
<td>47.8</td>
<td>R 29.4%</td>
<td>382</td>
<td>35.5</td>
<td>100</td>
</tr>
<tr>
<td>JRC-TIO-5</td>
<td>3 - 4</td>
<td>A 70.6%</td>
<td>259</td>
<td></td>
<td></td>
</tr>
<tr>
<td>JRC-TIO-6</td>
<td>58.0</td>
<td>R 240</td>
<td>20</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>JRC-TIO-7</td>
<td>108</td>
<td>A 197</td>
<td>35</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>JRC-TIO-8</td>
<td>93.2</td>
<td>A 155</td>
<td>51.7</td>
<td>98.6</td>
<td></td>
</tr>
<tr>
<td>JRC-TIO-9</td>
<td>95.2</td>
<td>A 197</td>
<td>31</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>JRC-TIO-10</td>
<td>100</td>
<td>A 169</td>
<td>35.5</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>JRC-TIO-11</td>
<td>76.6</td>
<td>R 200</td>
<td>63</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>JRC-TIO-12</td>
<td>98.7</td>
<td>A 153</td>
<td>41</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>JRC-TIO-13</td>
<td>71.1</td>
<td>A 237</td>
<td>33</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

A : anatase, R : rutile. Reaction condition; NO: 1000ppm, NH3: 1000ppm, O2: 2%, Ar balance, GHSV = 32000 h⁻¹

2.3 Mechanism of photo-SCR with NH3 over TiO2 photocatalysts

Figure 1 shows the EPR spectra of TiO2. After evacuation at 673 K, the signals are derived from the Ti3⁺ species (Fig. 1 (a)). There is little change in EPR signal by the exposure of NH3 to TiO2 in the dark. On the other hand, EPR signal changed drastically after photo-irradiation. New signals assignable to NH2 radical were detected together with signals assigned to Ti3⁺. These new signals were quite stable even after more than 1 hour at 123 K without photo-irradiation. However, these signals immediately vanished by the exposure to NO in the dark whereas the intensity of signals due to Ti3⁺ species increased. This suggests that 1) the photo-generated electron is trapped on Ti4⁺ to form Ti3⁺ and positive hole is captured by adsorbed NH3 species to convert to active NH2 radical, and that 2) NO in the gas phase attacks the NH2 radical on TiO2 rapidly. As both NH2 radical and NO are doublet state species, it follows that NH2 radical reacts with NO easily without irradiation. Moreover, the formation of a NH2NO intermediate was confirmed by FTIR spectroscopy after admittance of NO to TiO2 adsorbing NH3 under photo-irradiation (vide infra). As described above, the signals due to Ti3⁺ species increased in intensity after the introduction of NO. It seems that the electron transfer took place from the N atom of adsorbed NH3 to the Ti atom of TiO2 bulk. In other words, the photo-generated electron was trapped on Ti atom and the photo-generated hole was captured by the NH2 species derived from adsorbed NH3. As a result, the NH2 species converted to the active NH2 radical. On the other hand, the electron may move into inside of TiO2 bulk as a stable free electron. Before the exposure to NO, recombination took place between a part of Ti3⁺ species and the NH3 radical. On the other hand, after the exposure to NO, the electron could not recombine because of losing an opponent (NH2 radical). The electron was localized and stabilized in inside of TiO2, and the signals assigned to the Ti3⁺ species increased in intensity.
Figure 1 EPR spectra of TiO$_2$ (a) after pretreatment, (b) after introduction of NH$_3$ in the dark, (c) under photo irradiation and (d) after introduction of NO in the dark.

Figure 2 shows the time course of N$_2$ evolution rate of photo-SCR. NO conversion and N$_2$ selectivity attained to 100 % and 96 % respectively in the conventional fixed bed flow system (GHSV = 8,000 h$^{-1}$). The N$_2$ evolution rate gradually increased at the initial stage and reached a steady rate at 1.5 h. However, when the reaction gas (a mixture of NO/NH$_3$/O$_2$) was passed in the dark for 0.5 h, and then photo-irradiation was started, the N$_2$ evolution rate immediately jumped to the level of the steady rate.

This clearly indicates that the induction period shown in Fig. 2 is the time for saturation of the adsorption equilibrium of the reactant molecule. When NH$_3$ were passed for 1.5 h in the dark, then the gas was switched to a mixture of NO/O$_2$ and the photo-irradiation was started, N$_2$ was evolved. The N$_2$ evolution rate gradually decreased and the total amount of evolved N$_2$ was consistent with that of equilibrium adsorption of NH$_3$ on TiO$_2$. On the contrary, when a mixture of NO/O$_2$ were firstly passed and then switched to NH$_3$, neither N$_2$ nor N$_2$O was formed. These results suggest that NH$_3$ species adsorbed on Lewis acid site is excited by photo-irradiation and reacts with NO in the gas phase to produce N$_2$. Furthermore, this is supported by the fact that only $^{15}$N$^{14}$N was evolved in the photo-SCR of $^{15}$NO with $^{14}$NH$_3$ in the presence of O$_2$.22

The adsorbed species and intermediates of photo-SCR were identified by in situ FT/IR spectra (Fig. 3). After NH$_3$ adsorbed on TiO$_2$, the bands (1136, 1215, and 1599 cm$^{-1}$) due to adsorbed NH$_3$ species on Lewis acid site of TiO$_2$ appeared.39,41 The bands at 1599 and 1215 cm$^{-1}$ retained their intensity after evacuation (Fig. 3 (b)) and exposure to NO in the dark (Fig. 3 (c)). The bands due to adsorbed NH$_3$ decreased gradually in intensity with irradiation time. On the other hand, the band at 1624 cm$^{-1}$, which is assignable to the deformation vibration of H$_2$O$^{12}$, grew. Furthermore, new bands between 1400 and 1600 cm$^{-1}$ were observed and then disappeared. These new bands are assigned to the nitrosamide species (NH$_2$NO) by comparing the FT/IR spectrum of TiO$_2$ exposed with $^{14}$NO and NH$_3$ to that exposed with $^{15}$NO and NH$_3$.42

Fig. 3 FT-IR spectra of adsorbed species on TiO$_2$ in the photo-SCR with NH$_3$: (a) after introduction of NH$_3$, (b) after evacuation, (c) after introduction of NO in the dark, (d) under photo irradiation for 10 min, (e) for 30 min, (f) for 60 min, and (g) for 120 min.
These results indicate that the intermediate of photo-SCR is the nitrosamide species (NH$_2$NO) and the nitrosamide species is decomposed to N$_2$ and H$_2$O. Moreover, it was confirmed that the Ti$^{2+}$ species of TiO$_2$ reduced by H$_2$ was re-oxidized to the Ti$^{4+}$ species by exposure to O$_2$ easily even at room temperature using UV-Vis spectroscopy. On the basis of these results, we proposed Eley-Rideal type mechanism as follows (Scheme 2) \textsuperscript{24, 25}: 1) the NH$_3$ adsors on Lewis acid site of TiO$_2$, 2) the adsorbed NH$_3$ species is excited by photo-irradiation, 3) the excited species (NH$_2$ radical) reacts with NO in the gas phase to form the nitrosamide species (NH$_2$NO), 4) the nitrosamide species is decomposed to N$_2$ and H$_2$O, and 5) Ti$^{2+}$ site is re-oxidized by molecular oxygen.

According to the dependencies of the partial pressure of NO, NH$_3$, and O$_2$, the reaction rate ($r$) of photo-SCR is expressed as [Eq. (2)].

$$r = k P_{\text{NH}_3}^{0.0} P_{\text{NO}}^{0.5} P_{\text{O}_2}^{0.07} \tag{2}$$

Here, the rate constant, the partial pressure of NH$_3$, NO, and O$_2$ are abbreviated to $k$, $P_{\text{NH}_3}$, $P_{\text{NO}}$, and $P_{\text{O}_2}$, respectively. This equation indicates that NH$_3$ adsorbs strongly on TiO$_2$ (Step 1) and that re-oxidation of Ti$^{2+}$ to Ti$^{4+}$ (Step 5) proceeds rapidly. By comparing the obtained rate equation [Eq. (2)] with the rate equation derived from the proposed reaction mechanism by steady-state approximation, we concluded that Step 4, the decomposition of the nitrosamide species, is the rate-determining step of photo-SCR.

**Scheme 2** Reaction mechanism of photo-SCR with NH$_3$ over TiO$_2$.

2.4 Enhanced of activity by improving of lifetime of photo-activated species

An efficient charge separation promotes the chemical reactions competing with a recombination of the photo-generated electrons and holes. Einaga et al. reported that benzene as a model VOCs (volatile organic compounds) can be abated by total oxidation over TiO$_2$ photocatalyst effectively.\textsuperscript{45-47} However, the specific activity of TiO$_2$ is absolutely low. They reported that 120 ppm of benzene cannot be removed over TiO$_2$, but 80 ppm of benzene is efficiently decomposed to CO$_2$ and CO in the presence of H$_2$O vapor. This would be caused by the insufficient lifetime of charge-separated state over TiO$_2$. It is widely thought that the photo-generated electrons and holes are consumed by recombination much more rapidly than by the photocatalytic reaction and the recombination is the main reason of too short lifetime of the charge-separated state and resulting in low activity of TiO$_2$. Indeed, the half-life of charge-separated state of TiO$_2$ was estimated to be below 100 usec.\textsuperscript{46, 47} Up to now, the limit of the extended lifetime of charge-separated state is only several ten of nsec despite the careful effort. Therefore, in the case of photo-SCR over TiO$_2$, it seems that the half-life of NH$_2$ radicals, which are formed by capturing photo-generated positive holes, is below 100 psec and that the rate-determining step of photo-SCR is the reaction of NH$_2$ radical with NO to form the nitrosamide species (NH$_2$NO). However, as described above, the kinetic study indicated that the decomposition of the nitrosamide species (Step 4) is the rate-determining step of photo-SCR. This strongly suggests that the strongly adsorbed NH$_3$ on Lewis acid site of TiO$_2$ lengthened the lifetime of the charge-separated state by trapping hole and consequently the recombination of the photo-generated electrons and holes is inhibited. Figure 4 shows the decay curve of NH$_2$ radical signal recorded by EPR after irradiation stopped. All decay curves can be approximated to a hyperbolic curve, indicating that NH$_2$ radical is quenched by the secondary reaction between NH$_2$ radical and electron. The half-

![Fig. 4](image-url) Day curve decay of NH$_2$ radical and the approximated curve (liners) at (a) 113 K, (b) 123 K, (c) 133 K and (d) 143 K.

![Fig. 5](image-url) Arrhenius plots of the half-lives of NH$_2$ radical at each temperature (dot) and the approximated line (liner).

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life of NH₂ radical at reaction temperature of photo-SCR (323 K) is calculated to be 1.4 min by using Arrhenius equation (Fig. 5). Since this half-life of the NH₂ radical at 323 K is much longer than that of the charge-separated state of TiO₂ (< 100 psec), the concentration of NH₂ radical on the surface of TiO₂ increased and the activity of photo-SCR is enhanced. To best of our knowledge, the intermediate and active species having a longer lifetime such as the NH₂ radical has not been reported.

2.5 Mechanism of formation of NH₂ radical over TiO₂

On the basis of these results, we conclude that the photo-SCR over TiO₂ as a function of the incident light (action spectrum) and a UV-Vis spectrum of TiO₂. The band gap of this TiO₂ is estimated to be 3.28 eV (photo-excitation energy is 385 nm). The action spectrum is in good agreement with the UV-Vis spectrum of TiO₂ in the region of wavelength < 385 nm. Although TiO₂ is unable to absorb light at wavelengths > 385 nm, photo-SCR proceeds upon irradiation up to ca. 450 nm. The feature of this action spectrum is similar to the UV-Vis spectrum of N-doped TiO₂. In order to reveal whether a new energy level derived from adsorbed molecule is located between the HOMO and LUMO levels or not, density functional theory (DFT) calculations were employed. DFT calculations revealed that N 2p electron donor level is located between O 2p and Ti 3d when NH₂ species are formed on a TiO₂ surface by the dissociatively-adsorption of NH₃.27

Fig. 6 Action spectrum of photo-SCR (dot) and UV-Vis spectrum of JRC-TIO-11 (liner); reaction condition of action spectrum: NH₃: 1000ppm, NO: 1000ppm, O₂: 2%; flow rate: 100 ml/min.

On the basis of these results, we conclude that the photoactivation of NH₃ adsorbed on TiO₂ to NH₂ radical occurs through two paths as shown in Fig. 7. One is the electron transition from the valence band consisting of O 2p orbitals to the conduction band consisting of Ti 3d orbitals of TiO₂ under UV irradiation. The other is the direct electron transfer from N 2p of adsorbed NH₃ to Ti 3d. This N 2p electron donor level formed between O 2p and Ti 3d enables the photo-SCR to proceed even under visible light irradiation (400–450 nm). It can be thought that the expansion of the effective wavelength of TiO₂ by adsorption of NH₃, called here, “in situ doping”, is one of the factors for high activity of TiO₂ in the photo-SCR.

Many researchers reported that the “pre-doped” or “pre-modified” photocatalysts with metals or ions such as N-doped TiO₂ adsorb the visible light.48-51 However, there has been no report that the effective wavelength of photo-reaction is shifted to a longer wavelength by the formation of donor level derived from adsorbed molecule on the catalyst during a chemical reaction (“in situ doping”). Moreover, “in situ doping” was found not only in photo-SCR with NH₃ over TiO₂ but also in the photooxidation of alcohols over Nb₂O₅. The detail of the photooxidation of alcohols over Nb₂O₅ is described in the next section.

3. Photooxidation of alcohols with molecular oxygen over Nb₂O₅ catalysts

3.1 Oxidation of alcohol with molecular oxygen

Catalytic alcohol oxidation to carbonyl compounds is one of the most important chemical transformations used in the industrial chemistry and in organic syntheses.52-54 Non-catalytic methods with stoichiometric, toxic, corrosive and expensive oxidants such as Cl₂, dichromate, permanganate, and peroxy acids under stringent conditions of high pressure and/or temperature have been widely used for alcohol oxidations.52-55 In addition, these reactions are often carried out with high concentration of bases and environmentally unfriendly organic solvents. Therefore, much attention has been paid to the development of heterogeneous catalytic systems that use clean and atom efficient oxidants like molecular oxygen or H₂O₂ without organic solvents.55-56

Recently, the aerobic oxidation of alcohols was successfully carried out by using heterogeneous catalysts such as tetrabutylammonium persulfate (TPAP)/MCM-41,59 Ru/CeO₂,60 Ru-hydrotalcite,61 Ru/hydroxyapatite (Ru-HAP),62 [RuCl₃(p-cymene)]²⁺/activated carbon,63 Ru/Al₂O₃,64 Pd-hydrotalcite which requires the addition of pyridine,65 and Pd or Pt on activated carbon.65, 66 These systems require the use of organic solvents. Wu et al. reported on solvent-free aerobic oxidation of alcohols by Pd/Al₂O₃.67 However, the use of the noble metal, Pd is an essential requirement. Despite the advantage of using heterogeneous catalysts without organic solvents nor additives for oxidation of alcohols, few reports have appeared on the use of highly active solvent-free heterogeneous catalysts with only molecular oxygen as oxidant.

In this respect, photoreactions are promising processes and the development of photocatalysts is a subject that is now receiving noticeable attention. TiO₂ has been identified as one example of a practical and useful photocatalysts,68-71 and widely used in degradation of organic pollutants in air and water. However, in the most part of these reports, TiO₂ is used in vapor phase oxidations at high temperature,67 oxidation of only lower
alcohols,\textsuperscript{69, 70} oxidation using solvents such as benzene\textsuperscript{71} and a low selectivity to partial oxidized products due to excess photo-activation of target products which leads to deep oxidation. Zhao et al\textsuperscript{72-75} reported that the photooxidation of alcohols on TiO\textsubscript{2} could be dramatically accelerated without any loss of selectivity by adsorption of Bronsted acid and this effect by Bronsted acid results from the decomposition of the relatively stable side-on peroxyde promoted by the protons, which efficiently clean the catalytic Ti-OH\textsubscript{2} sites. However, this system requires the use of benzotri fluor ide as a solvent.

Recently, we found the photooxidation of alcohols to carbonyl compounds proceeded selectively at low temperature over Nb$_2$O$_5$ without organic solvents nor any additives (Table 3).\textsuperscript{74-76} Various metal oxides (SiO$_2$, MgO, Al$_2$O$_3$, ZrO$_2$, V$_2$O$_5$, Ta$_2$O$_5$, MoO$_3$, and WO$_3$) showed no activity and the activity of ZnO was very low. TiO$_2$ showed higher activity than Nb$_2$O$_5$, however, the Nb$_2$O$_5$ catalyst showed improved selectivity compared to TiO$_2$ at the same conversion level.\textsuperscript{74} Nb$_2$O$_5$ is suitable for selective oxidation. The photooxidation did not take place in the dark. Autooxidation proceeded when 1-phenylethanol, cyclohexanol and benzyl alcohol were irradiated without catalyst. This was due to the formation of radical species by the photo-decomposition of carbonyl compounds (Norrish Type I reaction) which were present as impurities in the alcohols (entries 1 to 3). Nb$_2$O$_5$ catalyst improved the conversions and/or selectivities to carbonyl compounds greatly. The less reactive primary alcohol, 1-pentanol was also photooxidized over the Nb$_2$O$_5$ catalyst. The Nb$_2$O$_5$ catalyst was reusable and showed the same conversion and selectivity without any pretreatment as the catalyst as prepared.

\subsection*{3.2 Mechanism of photooxidation of alcohol over Nb$_2$O$_5$}

The adsorbed species and intermediates of photooxidation were identified by \textit{in situ} FT/IR spectra of adsorbed cyclohexanol on Nb$_2$O$_5$. Figure 8 shows the FT/IR spectra of adsorbed cyclohexanol on Nb$_2$O$_5$. The bands at 1467 and 1452 cm$^{-1}$ were assigned to $\delta$(CH$_2$) and the bands at 1363 and 1347 cm$^{-1}$ were assigned to $\delta$(CH$_3$), respectively. The new bands at 1091 and 1126 cm$^{-1}$ appeared after the adsorption of cyclohexanol on Nb$_2$O$_5$. Therefore, these bands are assigned to the stretching mode of a C-O bond in the alcoholate species on the Nb$_2$O$_5$, because the formation of the alcoholate species by the adsorption of alcohol is usually accompanied by a shift of the stretching mode of a C-O bond to a higher wavenumber.\textsuperscript{77, 79} The change in FT/IR spectra by UV irradiation ($< 390$ nm) was shown in Fig. 9. The intensity of the band assigned to $\nu$(C-O) (around 1090 cm$^{-1}$) decreased as the irradiation time increased, whereas the bands assigned to $\nu$(C=O) (1676 cm$^{-1}$) and the symmetric-stretching of the carboxylic acid anion (1554 cm$^{-1}$) gradually grew. This result indicates that the alcoholate species on Nb$_2$O$_5$ was excited by photons and oxidized to carbonyl compounds. Interestingly, the carbonyl compounds were formed even under visible light irradiation ($> 390$ nm).

Figure 10 shows the EPR spectra of Nb$_2$O$_5$. A broad EPR signal around $g = 1.9$ was observed at 123 K (Fig. 9 (c)), when 1-pentanol was adsorbed on Nb$_2$O$_5$ under UV-irradiation. This broad signal at $g = 1.9$ was assignable to Nb$^{4+}$\textsuperscript{80, 81} and immediately disappeared by the exposure to O$_2$ in the dark, indicating that Nb$^{4+}$ was oxidized to Nb$^{5+}$ rapidly even at 123 K. On the other hand, when 1-pentanol was adsorbed on Nb$_2$O$_5$ under UV-irradiation at 77K, EPR signal ($g = 2.006$, $A_{hf} = 2.0$ mT, $A_{hf} = 4.4$ mT) assigned to alkyl radical species was observed (Fig. 11). These new signals were stable at 77 K without photo-irradiation, but disappeared at room temperature. The signal was restored by UV-irradiation at 77 K. Moreover, the signal did not change in the presence of O$_2$ even under UV-irradiation (Fig. 11 (f)).

### Table 3 Photooxidation of various alcohols over Nb$_2$O$_5$ with molecular oxygen \textsuperscript{4, 6}

<table>
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<tr>
<th>Entry</th>
<th>Substrate</th>
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<td>168</td>
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<td>(46) 36</td>
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<td>168</td>
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<td>(82) 82</td>
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<td>192</td>
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<td></td>
<td></td>
<td>84</td>
<td>(24) 14</td>
<td>(92) 4</td>
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</table>

\textsuperscript{4} Reaction conditions were as follows: alcohol (10 mL), Nb$_2$O$_5$ (100 mg), 323 K, under 0.1 MPa of O$_2$, O$_2$ flow rate (2 cm$^3$ min$^{-1}$): conversion and selectivity were determined by gas chromatography with an internal standard.

\textsuperscript{6} Figures in parentheses are the results of photochemical reaction without catalysts.

![Fig. 8 FT-IR spectra of adsorbed cyclohexanol on Nb$_2$O$_5$. (a) cyclohexanol was exposed to Nb$_2$O$_5$ for 1 h (physiosorption + chemisorption), (b) evacuated for 2 h (chemisorption), (c) difference spectrum (a)-(b): physiosorption. Nb$_2$O$_5$ was evacuated at 773 K for 1 h and oxidized at 773 K with 10.7 kPa of O$_2$ and then evacuated at 773 K for 1 h before FT-IR measurements.](image-url)
This indicates that the alkenyl radical species dose not react with O$_2$. Therefore, it is suggested that 1) the photo-formed electron is trapped on Nb$^{5+}$ to form Nb$^{4+}$ and positive hole is captured by alcolohate species to convert to active alkenyl radical, 2) the active alkenyl radical is dehydrogenated to carbonyl compound (the reduction of Nb$^{5+}$ to Nb$^{4+}$ takes place simultaneously), and 3) O$_2$ in the gas phase re-oxidizes Nb$^{5+}$ to Nb$^{6+}$.

On the basis of these results, we proposed the reaction mechanism as shown in Scheme 3. 1) Alcohol is adsorbed on Nb$_2$O$_5$ as alcoholate species, 2) Alcoholate adsorbed on Nb$_2$O$_5$ is activated by transferring an electron to the conduction band reducing Nb$^{5+}$ to Nb$^{4+}$ and leaving a hole on alcoholate, 3) the formed alkenyl radical is converted to carbonyl compound, 4) the product desorbs, and 5) the reduced Nb$^{4+}$ sites are re-oxidized by the reaction with O$_2$.

In this mechanism, oxygen anion radical species (O$_2^-$ and O$_3^-$), which are formed by irradiation over TiO$_2$ and often responsible for total oxidation, do not contribute to the photooxidation over Nb$_2$O$_5$. For instance, when Nb$_2$O$_5$ was irradiated in the presence of O$_2$, no EPR signal due to oxygen anion radical species was observed. This presumably explains why the photooxidation of alcohol to carbonyl compound proceeds selectively over the Nb$_2$O$_5$ catalyst.

Scheme 3 Reaction mechanism of alcohol photooxidation with molecular oxygen over Nb$_2$O$_5$

We carried out the photooxidation of 1-pentanol under the various concentration of 1-pentanol, O$_2$ and the different light intensity to determine each reaction order. On the basis of these
The rate constant, the substrate concentration, the light intensity, and the pressure of the oxygen are abbreviated to \( k, [S], I \) and \( P_{O_2} \), respectively. By comparing the obtained rate equation [Eq. (3)] with the rate equation derived from the proposed reaction mechanism by steady-state approximation, it is suggested that Step 3 or Step 4 is the rate-determining step of the photooxidation of alcohol over Nb\(_2\)O\(_5\). The alkenyl radical species was not obtained at 123 K, whereas Nb\(^{4+}\) was observed. This suggests that Step 3, the conversion of formed alkenyl radical to carbonyl compound took place even at 123 K because of a high reactivity of the alkenyl radical species. FT/IR spectra showed that the desorption of the carbonyl compounds remained on the surface of Nb\(_2\)O\(_5\) at room temperature, indicating that the desorption of the carbonyl compound was slow. Therefore, we concluded that the rate-determining step of the photooxidation of alcohol over Nb\(_2\)O\(_5\) is Step 4, the desorption process of the formed carbonyl compound.

### 3.3 Mechanism of formation of alkenyl radical over Nb\(_2\)O\(_5\)

Figure 12 shows the apparent quantum efficiency of photooxidation of 1-pentanol as a function of the wavelength of the incident light (action spectrum) and a UV-Vis spectrum of Nb\(_2\)O\(_5\). Although Nb\(_2\)O\(_5\) catalyst is not able to absorb visible light (> 390 nm), the photooxidation of 1-pentanol took place under irradiation up to ca. 480 nm. This result is consistent with the change in the FT/IR spectra under visible light irradiation and a red shift of the effective wavelength of photo-reaction is similar to that of photo-SCR over TiO\(_2\). In the case of photo-SCR over TiO\(_2\), we found that the adsorbed NH\(_3\) was photo-activated by the direct electron transfer from N 2p electron donor level formed between O 2p and Ti 3d of TiO\(_2\) to the conduction band.}

\[
r = k [S]^{0.19} P_{O_2}^{0.65}
\]

(3)

In order to investigate the formation of a new energy level derived form adsorbed molecule, DFT calculations were employed and showed that donor levels were generated between the HOMO and LUMO levels of Nb\(_2\)O\(_5\) by adsorbed alcohol on Nb\(_2\)O\(_5\) and that the electron transitions from O 2p donor level derived from the adsorbed alcoholate species to the conduction band of Nb\(_2\)O\(_5\) (Nb 4d orbitals) had lower energy than those from O 2p of Nb\(_2\)O\(_5\) (the conduction band) to Nb 4d.\(^{75}\) On the basis of these results, we concluded that the photooxidation of alcohol over Nb\(_2\)O\(_5\) takes place through the direct electron transfer from the O 2p orbital of adsorbed alcoholate species to the conduction band consisting of Nb 4d orbitals as shown in Fig. 13 ("in situ doping"). As a result of "in situ doping", the photooxidation of alcohol proceeded even under visible light irradiation.

![Fig. 12 Action spectrum of photooxidation of 1-pentanol (dot) and UV-Vis spectrum of Nb\(_2\)O\(_5\) (liner). Reaction conditions of the action spectrum were as follows: 1-pentanol (10 ml), Nb\(_2\)O\(_5\) (100 mg), 323 K, under 0.1 MPa of O\(_2\), O\(_2\) flow rate (2 cm\(^3\) min\(^{-1}\)).](image-url)

**Fig. 12** Action spectrum of photooxidation of 1-pentanol (dot) and UV-Vis spectrum of Nb\(_2\)O\(_5\) (liner). Reaction conditions of the action spectrum were as follows: 1-pentanol (10 ml), Nb\(_2\)O\(_5\) (100 mg), 323 K, under 0.1 MPa of O\(_2\), O\(_2\) flow rate (2 cm\(^3\) min\(^{-1}\)).

**Conclusions and outlook**

By means of UV-Vis, ESR, FT/IR with the aid of kinetic study and DFT calculations, the detailed reaction mechanisms of photo-assisted selective reduction of NO with NH\(_3\) (photo-SCR) over TiO\(_2\) and photooxidation of alcohol with O\(_2\) over Nb\(_2\)O\(_5\) were revealed and unique photo-activation mechanism by "in situ doping" in both photo-SCR and photooxidation of alcohol was demonstrated.

TiO\(_2\) acts as an effective catalyst for photo-SCR even at room temperature. In this photo-SCR system, the re-heating of catalyst bed is unnecessary because of their possibility of application at low temperatures. Thus, photo-SCR system can miniaturize the reactor. Moreover, in this photo-SCR system, TiO\(_2\) photocatalyst can activate NH\(_3\) effectively even in the presence of excess O\(_2\). Indeed, we found that TiO\(_2\) acts as an effective catalyst for photo-assisted selective catalytic oxidation of NH\(_3\) (photo-SCO: 4NH\(_3\) + 3O\(_2\) → 2N\(_2\) + 6H\(_2\)O).\(^{85-87}\) Although further improving the activity may be needed, it seems that this photo-SCO system can be used for removing unreacted NH\(_3\) in the SCR process and for removing NH\(_3\) from small and isolated source such as daily firm.

Photooxidation of alcohols to carbonyl compounds proceed selectively over Nb\(_2\)O\(_5\) without organic solvents. Nb\(_2\)O\(_5\) shows higher selectivity to partial oxidation product than that of commonly used TiO\(_2\) photocatalyst, and efficient conversion under a solvent-free condition.

In the case of photo-SCR over TiO\(_2\), a new electron donor (N 2p) was located between O 2p and Ti 3d by the adsorption of NH\(_3\) on TiO\(_2\). The direct electron transition from N 2p to Ti 3d took place to form NH\(_3\) radical species by visible light irradiation. As a result, the photo-SCR proceeded even under visible light irradiation. The high activity of TiO\(_2\) was caused by the expansion of the effective wavelength of TiO\(_2\) by adsorption of NH\(_3\) and the long lifetime of NH\(_3\) radical. In the case of
photooxidation of alcohol over Nb₂O₅, as well as the adsorbed NH₃ on TiO₂, the new electron donor level was generated between O 2p and Ti 3d by the adsorption of alcohol on Nb₂O₅. The direct electron transition from O 2p derived from alcohol to Ti 3d took place to form alkanyl radical species by photo-irradiation. Then, this alkanyl radical was immediately dehydrogenated to carbonyl compound. As shown in the present review, the unique photo-activation mechanism by “in situ doping” gives us attractive ways for the removing the limit of bandgap energy, and the utilization of visible light.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000xt
‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.