Propylene Oxide Synthesis and Selective Oxidation over Supported Metal Oxide Photocatalysts with Molecular Oxygen

Fumiaki Amano and Tsunehiro Tanaka

Abstract

Recent progress of photocatalytic epoxidation of propylene with molecular oxygen is reviewed. Highly dispersed metal oxide photocatalysts, such as silica-supported V$_2$O$_5$, Nb$_2$O$_5$, and TiO$_2$ with low loading, promote steady-state propylene oxide formation with high selectivity (>40%). The isolated tetrahedrally-coordinated species in the ligand-to-metal charge-transferred state is the photocatalytic active site. The photo-induced hole center localized on the lattice oxygen plays a significant role for the photocatalytic epoxidation. In the case of isolated TiO$_2$ tetrahedra on silica, an electrophilic oxygen species is generated by the reaction between the hole center and molecular oxygen. The addition of alkali ions to surface VO$_5$ tetrahedra improves the photocatalytic epoxidation ability of V$_2$O$_5$/SiO$_2$ with low loading. The key step in the selective photocatalytic oxidation over isolated VO$_5$ tetrahedra is the electron transfer from a hydrocarbon to the photo-induced hole center on the lattice oxygen, which is inserted in the photogenerated products.

1. Introduction

The use of solar energy as a reagent is an economically advantageous process for chemical conversion. A great deal of attention has been devoted to photocatalytic systems for activation of molecular oxygen in order to achieve selective oxygenation of organic molecules. There are two types of photocatalysts as shown in Figure 1, typically divided to inorganic semiconductor photocatalyst and organic photosensitizer photocatalyst.

When metal oxide particles as semiconductor absorb photon energies larger than the band gap, the photo-excited electrons and holes are produced in the conduction band and the valence band, respectively. An efficient charge separation promotes the chemical reactions competing with a recombination of the electrons and the holes. In the case of photosensitizer, an electron in the highest occupied molecular orbital (HOMO) is transferred to the lowest unoccupied molecular orbital (LUMO). The electronically excited state can act as stronger electron donor and acceptor than the ground state. The long-lived triplet state via intersystem crossing from the singlet state effectively promotes chemical reactions in competition with a radiative back-electron transfer to the ground state.

An attention of recent studies has been concentrated mainly on degradation and mineralization of pollutants using TiO$_2$ semiconductor photocatalysts. On the irradiated TiO$_2$ surface, many kinds of active oxygen species and radicals are present simultaneously, which lead to total oxidation of organic molecules to carbon dioxide. Therefore, a control of selective partial oxidation with molecular oxygen is difficult on conventional semiconductor photocatalysts.

Tanaka et al. found that highly dispersed niobium oxide species on silica are active for photoepoxidation of propylene in the presence of molecular oxygen at room temperature. Propylene oxide (PO) is a great important product in chemical industry. However, direct epoxidation of propylene by molecular oxygen, which is an ideal oxidant from the environmental and economic viewpoints, is difficult due to the high reactivity of the allylic C–H bonds. Recently, indirect epoxidation method by in situ generation of H$_2$O$_2$ from O$_2$ has been reported over titanosilicate-supported noble metals, although it is necessary to improve the utilization efficiency of the co-feeding hydrogen and the production rate of PO. The excellent work by Yoshida and co-workers shows that many kinds of highly dispersed metal oxide species on silica exhibit ability to PO formation in the photooxidation of propylene using O$_2$. Such a direct photoepoxidation of lower alkenes has not been reported in any other photocatalysts except for the highly dispersed metal oxide photocatalysts.

2. Photoepoxidation of Propylene over Supported Metal Oxide

Strategies for the design of a photocatalyst for partial oxidation are to control the number and the kinds of active oxygen species and create a catalytic site for a selective reaction with the reactant molecules. An atomically dispersed metal oxide species on silica would be recognized as a mononuclear complex attached to the surface. This species exhibits the property of pho-
tosensitizer photocatalyst rather than semiconductor photocatalyst. Photoexcitation causes a charge transfer from the oxygen ligand to the metal cation (LMCT transition). Since silica is an insulator, the photo-induced electron and hole are localized on the isolated metal oxide species. This charge-transferred excited state with a hole center trapped on the lattice oxygen and an electron on the metal cation would be favorable for promoting selective reaction, such as partial oxidation.\(^7\)

On the basis of this concept, two types of Nb\(_2\)O\(_5\)/SiO\(_2\) were prepared by an equilibrium adsorption method (type A, 0.2 wt % as Nb\(_2\)O\(_5\)) and conventional evaporation to dryness method (type E). The type A catalyst contains monomeric NbO\(_4\) tetrahedra, and type E catalyst both monomeric and oligomeric NbO\(_4\) tetrahedra. As shown in the phosphorescence decay curves (Figure 2), type A catalyst exhibits long-lived emission species.\(^4\) By a contact with propylene, the emission was quenched more efficiently for type A than for type E catalyst. This indicates that the monomeric NbO\(_4\) tetrahedra in the excited triplet state preferentially interact with propylene. The type A exhibits higher selectivity and activity for PO formation than the type E catalyst in the photooxidation over the highly dispersed metal oxide clusters.\(^7\)

A series of highly dispersed transition-metal oxides such as TiO\(_2\),\(^9,10\) ZnO,\(^11\) and CrO\(_2\)\(^12\) in and on SiO\(_2\), have also been found to promote photoepoxidation of propylene with high selectivity (60% for TiO\(_2\)–SiO\(_2\)).\(^9,10\) It has been reported that the TiO\(_2\)–SiO\(_2\) could be extended to other light alkenes such as ethylene and butenes. In general, the active sites for photooxidation exist in an isolated state with tetrahedral coordination.\(^7\) The selectivity in the photooxidation over the highly dispersed metal oxides is significantly different from that over the corresponding metal oxide clusters. The typical semiconducting photocatalysts (TiO\(_2\) and ZnO) predominantly promote the total oxidation to CO\(_2\) in the photocatalytic oxidation of propylene.\(^13,14\) Although trace amounts of PO and propanal were produced at the extremely low conversion level, the unstable products are consecutively decomposed. In the case of higher alkenes such as 2-hexene, photocatalytic epoxidation was promoted over TiO\(_2\) and Ti-containing SiO\(_2\) using molecular oxygen.\(^15,16\)

### 3. Photocatalytic Epoxidation of Propylene over V\(_2\)O\(_5\)/SiO\(_2\)

It is well known that the isolated VO\(_4\) tetrahedra supported on SiO\(_2\) exhibit photoactivity for oxidation from the photoluminescence studies.\(^7\) Figure 3 shows the phosphorescence spectra of the dehydrated V\(_2\)O\(_5\)/SiO\(_2\) at a liquid nitrogen temperature. The lifetime of the emission was about 10 ms. The vibrational fine structure of the emission is attributed to the stretching of the terminal vanadyl V=O bond\(^17\) or the basal V–O–Si bonds.\(^18\) It is generally accepted that the triplet emission state involves an intersystem crossing from the singlet excited state localized on monooxo-vanadium group. The promotion of an electron into the antibonding orbital of the V=O bond (\(n \rightarrow \pi^*\) transition) destabilizes and activates the lattice terminal oxygen that is responsible for the photooxidation of CO (lattice oxygen insertion). Tanaka et al. examined the photooxidation of propylene with molecular oxygen over the V\(_2\)O\(_5\)/SiO\(_2\).\(^19,20\) The products were ethanol, propenal, and propanal. However, PO was not detected although the formation of PO had been predicted as a precursor to propanal.\(^20\)

The previous studies on the propylene photooxidation estimated the activity of highly dispersed metal oxide photocatalysts using a closed reactor system.\(^4,6,9,12,19-21\) The long contact time is disadvantage on the decomposition of the unstable intermediates. Moreover, it is unclear that the photo-assisted synthesis of PO is really “catalytic” reaction. Therefore, a flow reactor was adopted instead of a conventional closed reactor.\(^22-24\)

Figure 4 shows the results of the photocatalytic epoxidation of propylene over V\(_2\)O\(_5\)/SiO\(_2\) with different vanadium loadings. Using a flow system, the selective formation of PO over the isolated VO\(_4\) tetrahedra on silica could be observed for the first time.\(^22\) At 303 K, the conversion rate of propylene was maximized on the 0.1 wt % loaded catalysts (0.01 V-atom nm\(^{-2}\)). The selectivity to PO reached 40% and decreased with an increase in the loading amount. The decrease in the propylene conversion is because of a suppression of the desorption of the photogenerated PO from the catalyst surface due to the acid sites, the number of which is linearly increased with the V\(_2\)O\(_5\) loading.

---

**Figure 2.** Phosphorescence emission decay curves of Nb\(_2\)O\(_5\)/SiO\(_2\) prepared by an equilibrium adsorption method (type A) and a conventional evaporation to dryness method (type E).

**Figure 3.** Diffuse reflectance UV–vis spectrum and photoluminescence spectra of 0.5 wt % V\(_2\)O\(_5\)/SiO\(_2\) at dehydrated state. The phosphorescence excitation and emission spectra were recorded by monitoring at 530 nm and excitation at 320 nm, respectively.

**Figure 4.** Concentration of PO and propanal evolution over V\(_2\)O\(_5\)/SiO\(_2\).
By heating the catalysis bed to 473 K during the photocatalysis, the conversion rate of propylene was significantly increased at the higher loading region than 0.1 wt%. Up to the loading amount < 2.5 wt%, the samples consist of a monomeric VO₂ tetrahedral species dispersed on SiO₂. Therefore, the isolated (SiO₂)VO₂ species is the photocatalytic active site for PO formation. In the case of highly loaded VO₂/SiO₂, propanal was selectively produced instead of PO (the selectivity to propionaldehyde as a secondary product via PO). This indicates that propionaldehyde is a secondary product via PO. The isomerization of PO over vanadium oxide species on SiO₂ has been confirmed as a secondary product via PO. The isomerization of PO over vanadium oxide species on SiO₂ has been confirmed under thermal treatment in a closed circulation reactor.

The catalysts, such as Nb₂O₅/SiO₂, MgO/SiO₂, TiO₂/SiO₂, ZnO/SiO₂, and Cr₂O₃/SiO₂ have been reported as effective for photoepoxidation of propylene in a closed reactor. Photocatalytic epoxidation of propylene with O₃ at room temperature was investigated over various silica-supported metal oxides with low loading in a flow reactor. Table 1 shows the results of the photocatalytic epoxidation of propylene after 5 h of time on stream. The high PO yield was achieved over the V, Ti, and Nb oxides on silica. Amorphous silica was more effective than FSM-16 for supported Ti and V oxides. The decrease of PO production is presumably because of the acid properties of FSM-16 silica. Bulk TiO₂, semiconductor photocatalyst, promotes the deep oxidation under UV irradiation.

Figure 5 shows the time-dependent behavior of the photocatalytic epoxidation of propylene at 303 K. The conversion rate of propylene and the formation rate of PO were increased in the order Nb < Ti < V oxides on silica. The selectivity to PO at steady state was very stable during the reaction. In the case of Cr₂O₃/SiO₂, a gradual deactivation was observed with the course of the reaction, although the initial activity was detected.

4. Mechanism of Photocatalytic Epoxidation

The oxidation state and the coordination environment of the supported Ti, V, and Cr oxide species were determined by diffuse reflectance UV–vis spectroscopy and electron spin resonance (ESR). During the photocatalytic oxidation, the active oxygen species on TiO₂/SiO₂, TiO₂/SiO₂, ZnO/SiO₂, and Cr₂O₃/SiO₂ have been reported as effective for photoepoxidation of propylene in a closed reactor. Photocatalytic epoxidation of propylene with O₃ at room temperature was investigated over various silica-supported metal oxides with low loading in a flow reactor. Table 1 shows the results of the photocatalytic epoxidation of propylene after 5 h of time on stream. The high PO yield was achieved over the V, Ti, and Nb oxides on silica. Amorphous silica was more effective than FSM-16 for supported Ti and V oxides. The decrease of PO production is presumably because of the acid properties of FSM-16 silica. Bulk TiO₂, semiconductor photocatalyst, promotes the deep oxidation under UV irradiation.

Figure 5 shows the time-dependent behavior of the photocatalytic epoxidation of propylene at 303 K. The conversion rate of propylene and the formation rate of PO were increased in the order Nb < Ti < V oxides on silica. The selectivity to PO at steady state was very stable during the reaction. In the case of Cr₂O₃/SiO₂, a gradual deactivation was observed with the course of the reaction, although the initial activity was detected.

Table 1. Results of photooxidation of C₃H₆ with O₂ at 303 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion /µmol h⁻¹</th>
<th>PO yield /µmol h⁻¹</th>
<th>Selectivity/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂/SiO₂</td>
<td>36</td>
<td>18</td>
<td>50</td>
</tr>
<tr>
<td>V₂O₅/SiO₂</td>
<td>69</td>
<td>26</td>
<td>37</td>
</tr>
<tr>
<td>Nb₂O₅/SiO₂</td>
<td>31</td>
<td>12</td>
<td>40</td>
</tr>
<tr>
<td>Cr₂O₃/SiO₂</td>
<td>3</td>
<td>1</td>
<td>42</td>
</tr>
<tr>
<td>ZnO/SiO₂</td>
<td>3</td>
<td>2</td>
<td>62</td>
</tr>
<tr>
<td>MgO/SiO₂</td>
<td>2</td>
<td>1</td>
<td>74</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2</td>
<td>1</td>
<td>73</td>
</tr>
<tr>
<td>TiO₂ (JRC-TIO-4)</td>
<td>67</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>TiO₂/FSM-16</td>
<td>19</td>
<td>7</td>
<td>35</td>
</tr>
<tr>
<td>V₂O₅/FSM-16</td>
<td>49</td>
<td>4</td>
<td>8</td>
</tr>
</tbody>
</table>

-a Catalyst 0.3 g, Total flow rate 100 mL min⁻¹, Reactants: 20% C₃H₆, 10% O₂, 70% He, Irradiation 240 < λ < 440 nm, Reaction temperature 303 K. The data were obtained at 300 min on stream.

Figure 4. Effect of V₂O₅ loading on the conversion rate of propylene and the selectivity to PO in the photooxidation of C₃H₆ with O₂ over V₂O₅/SiO₂ in a flow reactor. Catalyst 0.3 g, Total flow rate 100 mL min⁻¹. Reactants: 20% C₃H₆, 10% O₂, 70% He. Irradiation 240 < λ < 440 nm. Reaction temperature 303 and 473 K.

Figure 5. Time course of the photooxidation of C₃H₆ with O₂ over 0.1 mol % TiO₂/SiO₂, V₂O₅/SiO₂, Cr₂O₃/SiO₂, and Nb₂O₅/SiO₂. Catalyst 0.3 g. Total flow rate 100 mL min⁻¹. Reactants: 20% C₃H₆, 10% O₂, 70% He. Irradiation 240 < λ < 440 nm. Reaction temperature 303 K.
assigned to isolated Cr photo-induced hole center on the mono-hydroxyl (SiO) 

tice oxygen directly reacts with propylene. On the contrary, a oxidation by molecular oxygen even at 673 K. Although the visible light, 12,26 the photoreaction is stoichiometric rather than oxidation.

photo-activated lattice oxygen has capability for propylene photocatalytic (Figure 6c). Since there is an initial activity, the 

indicates oxygen atom originated from lattice oxygen. 

desirable side reactions. Recently, Shiraiishi et al. found that an addition of acetonitrile suppresses the electron transfer from alkenes to hole center on Ti-containing silica and improves the epoxide selectivity in the photooxidation of higher alkenes.16

In the case of V2O5/SiO2, the photo-activated oxo ligand is the active oxygen species for PO production.24 The lattice oxygen in the excited triplet state, (V330δ−δ=O), is considered to exhibit electrophilic character, which attacks the double bond in propylene. On the contrary to TiO2/SiO2, the electron transfer from propylene to the hole center would form an epoxide-like intermediate attached to the lattice oxygen. The V3+ cation trapping an electron will be oxidized by oxygen molecule.

Figure 7 shows ESR spectra of CrO3/SiO2 24 When the sample was irradiated with 20 Torr of C3H6 and 10 Torr of O2 for 1 min, axial symmetric γ-signal due to Cr6+(d3) was immediately increased and gradually decreased with an increase of broad δ-signal characterized by a positive lobe, which is assigned to isolated Cr5+(d3) species. This indicates that the Cr6+ species was successively reduced to photo-inactive species such as Cr5+ and Cr4+. The reduced species resisted to the reoxidation by molecular oxygen even at 673 K. Although the CrO3/SiO2 is attractive material for photooxidation using visible light,12,26 the photoreaction is stoichiometric rather than photocatalytic (Figure 6c). Since there is an initial activity, the photo-activated lattice oxygen has capability for propylene oxidation.

In the case of the monooxo (SiO)3V=O and dioxo (SiO)2Cr(=O)2 species, a photo-induced hole center on the lattice oxygen directly reacts with propylene. On the contrary, a photo-induced hole center on the mono-hydroxyl (SiO)3Ti-OH

Figure 6. Proposed reaction mechanisms in the C3H6 photooxidation with O2 over (A) TiO2/SiO2, (B) V2O5/SiO2, and (C) CrO3/SiO2, where R is propylene and RO is propylene oxide. The O indicates oxygen atom originated from lattice oxygen.

Figure 7. ESR spectra of 0.1 mol % CrO3/SiO2 at room temperature (A) and 123 K (B). The spectra were recorded after calcination and outgassing at 673 K (a), irradiation in the presence of 20 Torr C3H6 and 10 Torr O2 for 1 min (b), 10 min (c), and 30 min (d) at room temperature and outgassing.

species activates O2 to electrophilic oxygen species (T-type O3−). It is suggested that the kinds of the terminal ligand (hydroxyl or oxo) of the tetrahedrally coordinated metal oxides on silica decide the kinds of active oxygen species in the photocatalytic oxidation.

5. Modification of Photocatalytic Center of V2O5/SiO2

Among the highly dispersed metal oxides, the vanadium oxide species anchored on silica shows the highest photocatalytic activity.24 Moreover, it is possible to enhance the photooxidation ability of V2O5/SiO2 by an alkali ion addition.27,28 The alkali ion interacts to the terminal oxo of the monomeric VO2 tetrahedron on silica. Amano and Tanaka tried the modification of the electronic state of the photocatalytic center, the photo-excited lattice oxygen, by an alkali ion addition in order to achieve further improvement of the PO formation rate.23 The photooxidation of propylene with O2 was investigated over alkali-ion-modified V2O5/SiO2 at low vanadium loading. The addition of Rh+ ions to 0.5 wt % V2O5/SiO2 resulted in the great improvement of the formation rate of PO.23 Alkali ions of Li+, Na+, K+, and Cs+ gave the similar effect upon the photocatalysis. The photocatalytic performances of Rh-ion-modified V2O5/SiO2 are summarized in Table 2. The propylene conversion and the PO selectivity over Rh-ion-modified V2O5/SiO2 (Rh/V molar ratio = 0.5–3.0) are higher than that of non-modified V2O5/SiO2. The photocatalytic activity was significantly enhanced when the Rh/V value varied from 0.5 through 1.0. Because the pH value of the solution used for catalyst preparation is high, the specific surface area of Rh-ion-modified V2O5/SiO2 was reduced with an increase in the amount of Rh addition. The higher Rh-ion-addition drastically decreased the PO formation rate due to an enhancement of non-selective oxidation to CO2.

Figure 8 shows diffuse reflectance UV–vis spectra of Rh-ion-modified V2O5/SiO2.23 The color of V2O5/SiO2 was yellowish green at hydrated state. The band observed around 400 nm is assigned to the LMCT transitions of the V2O5-like polymerized species. It is known that the tetrahedral VO3 monomers on silica at dehydrated state are changed to square pyrami-
Table 2. Results of photooxidation of C\textsubscript{3}H\textsubscript{6} with O\textsubscript{2} over Rb-ion-modified 0.5 wt % V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2}\textsuperscript{a}

<table>
<thead>
<tr>
<th>Rb/V</th>
<th>S\textsubscript{BET}\textsuperscript{b} / m\textsuperscript{2} g\textsuperscript{-1}</th>
<th>TOS\textsuperscript{c} / min</th>
<th>Conversion /%</th>
<th>Selectivity /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>588</td>
<td>180</td>
<td>0.4</td>
<td>14</td>
</tr>
<tr>
<td>0.5</td>
<td>510</td>
<td>60</td>
<td>0.6</td>
<td>28</td>
</tr>
<tr>
<td>1</td>
<td>485</td>
<td>60</td>
<td>1.4</td>
<td>31</td>
</tr>
<tr>
<td>1.5</td>
<td>348</td>
<td>60</td>
<td>1.6</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>296</td>
<td>60</td>
<td>1.5</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>191</td>
<td>60</td>
<td>1.0</td>
<td>9</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Catalyst 0.3 g. Total flow rate 25 mL min\textsuperscript{-1}. Reactants: 20% C\textsubscript{3}H\textsubscript{6}, 10% O\textsubscript{2}, 70% He. Irradiation 240 < \lambda < 440 nm. Reaction temperature 303 K. \textsuperscript{b}BET specific surface area. \textsuperscript{c}Time on stream.

6. Selective Photooxidation over Supported Metal Oxide Photocatalysts

The highly dispersed vanadium oxide species promotes the selective photooxidation of alkanes as well as alkenes with O\textsubscript{2}.\textsuperscript{28,32,33} Gas-phase selective oxidation of light alkanes is important for the usage of natural gas and liquefied petroleum gas. Tanaka et al. have reported that alkali-ion-modified V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} is available for selective photocatalytic oxidation of propane and butanes at room temperature.\textsuperscript{28} At elevated reaction temperature, 493 K, Wada et al. reported the selective photo-assisted oxidation of methane to formaldehyde using V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} photocatalyst.\textsuperscript{32} In the case of liquid-phase reaction, silica-supported vanadium oxide is not effective due to the leaching, and V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3} exhibits high photocatalytic activity for partial oxidation of hydrocarbons such as cyclohexane in the presence of O\textsubscript{2} at room temperature.\textsuperscript{33}

The photocatalytic oxidation mechanism has been investigated for acetone formation from propane.\textsuperscript{34,35} The photocatalyst system with Rb-ion-modified V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} can be operated without deactivation at a high rate of the acetone production in a flow reactor.\textsuperscript{30} The active oxygen species is not derived from molecular oxygen but from the lattice oxygen of the VO\textsubscript{4} species interacted with Rb ion.\textsuperscript{34} The kinetic analysis demonstrated that the rate-determining step is the reaction of propane with the photo-induced hole center on the lattice oxygen of the Rb-ion-modified VO\textsubscript{4} species to yield the vanadium isopropoxide species.\textsuperscript{35} Heating the photocatalyst bed drastically enhanced not only the yield of acetone but also the yield of propanal that is a minor product in the photooxidation at 333 K. Figure 9 shows the logarithm plots of the formation ratio of acetone to propanal (R\textsubscript{ACT}/R\textsubscript{PA}) against the reciprocal of the reaction temperature in the photooxidation of propane.\textsuperscript{35} A linear relationship suggested that the formation ratio of the precursor into acetone to the precursor into propanal obeys Boltzmann’s distribution of the stabilizing energy difference between the precursors, \Delta E. The ratio is expressed as follows.

\[
\frac{R_{\text{ACT}}}{R_{\text{PA}}} = \exp \left( \frac{\Delta E}{RT} \right),
\]

where $R$ is the gas constant and $T$ is the reaction temperature. The precursors to acetone and propanal are assumed to be an vanadium isopropoxide-like intermediate and an vanadium n-propoxide-like intermediate, respectively. The stabilizing energy difference was estimated to be 11.4 kJ mol\textsuperscript{-1} by a slope of Figure 9, which is nearly consistent with the result of DFT calculation of the assuming intermediates (14.1 kJ mol\textsuperscript{-1}).\textsuperscript{35} Therefore, it is concluded that the product distribution of the photo-assisted oxidation of propane is described by the stabilization energy difference of the photo-adsorbed propane species that is attached to the lattice oxygen of vanadium species.

7. Summary

V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} and alkali-ion-modified V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} were found to be promising photocatalysts for PO formation in the photooxidation of propylene with O\textsubscript{2} and TiO\textsubscript{2}/SiO\textsubscript{2} exhibits excellent
selectivity to PO at fairly high conversion. In the case of V₂O₅-based catalysts, the active oxygen is the lattice oxygen while in the case of TiO₂-based catalysts, it is adsorbed molecular oxygen. However, interestingly, both of the active oxygen species are electrophilic, suggesting that a key step is the electron transfer from a hydrocarbon to an active oxygen species as a photo-induced hole center. As shown in the present review, the kinds and the property of the active oxygen species can be controlled over highly dispersed metal oxide photocatalysts for selective partial oxidation.

References