Selective Photocatalytic Oxidation of Light Alkanes over Alkali-Ion-Modified V₂O₅/SiO₂; Kinetic Study and Reaction Mechanism

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Alkali-ion-modified silica-supported vanadium oxides are photocatalysts available in the field of photooxidation of light alkanes using molecular oxygen. The photooxygenated reaction was promoted over the catalyst under irradiation at steady state. Acetone formation on the photooxidation of propane was investigated over a rubidium-ion-modified silica-supported vanadium oxide that is the most effective catalyst. The kinetic analysis demonstrated that the rate-determining step is the reaction of propane on the lattice oxygen of the photoexcited VO_4Rb species to yield the vanadium isopropoxide species. It was suggested that the photocatalytic active sites are occupied by photogenerated acetone during photoreaction at 333 K. Heating the photocatalyst bed drastically enhanced not only product yield but also the selectivity to propionaldehyde that is a minor product in the photooxidation at 333 K. The product distribution of photoassisted oxidation of propane was described by Boltzmann's distribution of stabilization energy of the intermediates: an isopropoxide-like one for the precursor of acetone and an *n*-propoxide-like one for the precursor of propionaldehyde.

Introduction

Gas-phase selective oxidation of light alkanes is important for the usage of natural gas and liquefied petroleum gas. However, selective conversion to partial oxidative products is difficult due to the low chemical reactivity of light alkanes. One of the candidates for the selective oxidation is photooxidation of hydrocarbons over heterogeneous photocatalysts.^{1,2} Frei et al. demonstrated the formation of alkane-oxygen chargetransfer pairs in the cavities of alkaline-earth ion-exchanged zeolites under visible light irradiation.³⁻⁵ Highly selective oxidation of propane into propanone (acetone) proceeded in the zeolites under irradiation as well as dark conditions.⁴⁻⁸ Another example for photocatalytic oxidation of alkanes is an alkaliion-modified vanadium oxide supported on silica (V_2O_5 / SiO₂).^{9–16} It is widely known that V₂O₅/SiO₂ possesses photocatalytic activity since the publication of the photoluminescence study.^{17–19} V₂O₅/SiO₂ promotes the partial oxidation of methane into formaldehyde under photoassisted thermal conditions.²⁰⁻²² Also reported is the photoreaction of nitrogen monoxide with propane, leading to the formation of N₂, propylene, acetone, and CO₂ at room temperature.^{23,24} At low loading with vanadium oxide, photoepoxidation of propylene into propylene oxide using molecular oxygen is catalyzed.^{25,26}

We have reported that the addition of alkali ions to V_2O_5/SiO_2 resulted in enhancement of the photocatalytic activity, utilization of visible light, and improvement of the production selectivity.¹⁰⁻¹⁴ The photocatalytic reaction selectivity over alkali-ion-modified V_2O_5/SiO_2 was quite different from that over thermally activated catalyst; a secondary carbon is preferentially oxidized rather than an olefinic bond.¹⁶ The photocatalyst system with rubidium-ion-modified V_2O_5/SiO_2 can be operated without deactivation at a high rate of production of partial oxidation products of propane and butane; the saturated secondary carbon is selectively attacked, and the ketones are formed at steady state.^{15,16} These findings motivated us to investigate the reaction

mechanism of photooxidation of light alkanes over alkali-ionmodified V_2O_5/SiO_2 . The present paper reports kinetic studies for the photooxidation of propane in a flow reactor system. The conclusion leads to improvement of the catalytic activity and identification of main factors for the product selectivity.

Experimental Section

Catalyst Preparation. Silica was prepared by hydrolysis of distilled tetraethyl orthosilicate in a water—ethanol mixture at the boiling point, followed by calcination in dry air at 773 K for 5 h. The V₂O₅/SiO₂ was prepared by impregnation of silica with an aqueous solution of NH₄VO₃, followed by evaporation to dryness and calcination in dry air at 773 K for 5 h. The loading amount of vanadium was adjusted to be 2.5 wt % as V₂O₅. The alkali-ion-modified catalyst was prepared by impregnation of V₂O₅/SiO₂ with an aqueous solution dissolving the necessary amount of RbOH (Rb/V = 1.5 as molar ratio), followed by calcination in dry air at 773 K. The rubidium-ion-modified V₂O₅/SiO₂ is denoted as Rb-VS.

Photocatalytic Reactions. The catalyst powder (300 mg, 50-70 mesh) was diluted with 4.5 g of quartz granular (20-28)mesh) and was mounted on a catalyst bed (3.0 mL) made of Pyrex glass. Pretreatment of the catalyst was carried out by heating at 673 K under an atmospheric stream of He/O₂ (80: 20) mixture at a flow rate of 100 mL min⁻¹. A reaction was carried out under a total flow rate of 100 mL min⁻¹ of a gas mixture of propane, oxygen, and helium (20:10:70) at atmospheric pressure. The reactor was irradiated by a 300-W xenon arc lamp (Perkin-Elmer PE300BUV) through a glass filter (Asahi techno glass UV31) which can permit UV-vis light with $\lambda > 300$ nm. The products were analyzed by gas chromatographs (a PEG 20M column with a flame ionization detector and a Shincarbon T column with a thermal conductivity detector) connected directly to a flow reactor. During the irradiation, the temperature of the catalyst bed was 333 K, measured by an infrared radiation thermometer.

Spectroscopies. Diffuse reflectance UV-vis spectra were obtained using a Perkin-Elmer Lambda-19 spectrometer equipped

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Figure 1. Photoluminescence spectra of Rb-VS. The phosphorescence excitation spectrum was monitored at 530 nm, and the phosphorescence emission spectrum was excited at 390 nm.

with an integrating sphere at room temperature. BaSO₄ was used as a standard reflection sample. Photoluminescence measurements were performed using a Hitachi F-3010 spectrometer at liquid-nitrogen temperature. The emission and excitation spectra were recorded at phosphorescence mode (delay time, 1 ms). Prior to each measurement, the samples were dehydrated by oxidation treatment at 673 K in a stationary quartz cell, evacuation for 30 min, oxidation with 50 Torr O₂ for 1 h, and evacuation for 30 min. The samples were measured without exposure to the open air after oxidation treatments.

FT-IR spectra were obtained using a Perkin-Elmer Paragon 1000PC spectrometer in transmission mode at room temperature. A 40-mg portion of the catalyst was pressed into a self-supporting wafer and mounted in an in-situ cell equipped with NaCl windows. The wafer was pretreated in the same way as the oxidation treatments for other spectroscopy measurements. The FT-IR spectra of adsorbed acetone were recorded with a resolution of 4 cm⁻¹.

Method of Calculations. The energy calculations of 1-propanol and 2-propanol were carried out on the basis of the hybrid Hartree–Fock/density functional theory (HF/DFT) B3LYP method using the Gaussian 03 ab-initio program package.²⁷ The B3LYP method consists of the Slater exchange, Hartree–Fock exchange, exchange functional of Becke, correlation functional of Lee, Yang, and Parr (LYP), and correlation functional of Vosko, Wilk, and Nusair (VWN). The geometries were fully optimized until a stationary point on the potential surface was found using a 6-31G basis set. The single-point energies of the optimized structures were calculated using a 6-311+G(d,p) basis set.

Results

Among the alkali ions (Na⁺, K⁺, and Rb⁺), Rb⁺ is the most striking for the additive effects to V₂O₅/SiO₂ for the photocatalytic performance of photooxidation of propane, 2-methylpropane, and *n*-butane.^{10,11,13–15} Rb-VS exhibits the highest and most stable activity for catalytic photooxidation of propane at steady state.¹⁵ The major products were acetone and CO₂ at 333 K.

Photocatalytic Active Site. Figure 1 shows phosphorescence spectra of Rb-VS (2.5 wt % as V_2O_5 , Rb/V = 1.5 as molar ratio). The phosphorescence excitation spectrum was consistent with the action spectrum of apparent photoefficiency in the photooxidation of propane over Rb-VS estimated assuming that the formation of one molecule of acetone requires one photon.¹⁵

The structure and the electronic state of Rb-VS have been investigated.^{28,29} Scheme 1 shows the proposed structure of the vanadium species of Rb-VS at ground state and photoexcited triplet state. The local structure of the vanadium species is a



Figure 2. Effect of propane pressure on the formation rate of acetone in photooxidation of propane over Rb-VS. The solid curve was a least-squares fitting by using the rate equation of eq 6 obtained from kinetic study.

SCHEME 1: Proposed Structures of Vanadium Species in Rb-VS at Ground State and Lowest Triplet State



VO₄ tetrahedron, two V–O bonds of which are interacted with an alkali ion.²⁸ The presence of an alkali ion causes the elongation of the V=O and V–O bonds of a mononuclear (V=O)O₃ tetrahedron and red shift of the wavelength of the phosphorescence excitation in V₂O₅/SiO₂. The excitation to triplet state via intersystem crossing from an excited singlet state is assignable to the transition from the nonbonding orbital of oxygen atoms interacted with an alkali ion at ground state to a π^* -like molecular orbital.²⁹ The semi-occupied orbital formed by excitation was proposed to be the photocatalytic site for alkane oxidation, that is, the electron of the highest occupied molecular orbital (HOMO) of the alkane is transferred to the site.

Kinetic Study of the Photocatalytic Reaction. The result obtained from the previous adsorption study is summarized as follows: (a) oxygen by itself is not adsorbed on Rb-VS, (b) propane is adsorbed under irradiation, and (c) oxygen is adsorbed on Rb-VS having adsorbed propane.^{11,29} The mechanistic study so far suggests an Elley–Rideal mechanism in the photooxidation of light alkanes over Rb-VS.

Figure 2 shows the result of propane pressure change in photooxidation of propane over Rb-VS. The formation rate of acetone monotonically increased with an increase in propane pressure. Figure 3 shows a linear relationship in log-log plots of the formation rate of acetone versus propane pressure. The acetone formation rate is expressed as follows:

$$\log R_{\text{ACT}} = 0.4 (\log P_{\text{C}}) + \log k$$
$$R_{\text{ACT}} = k P_{\text{C}}^{0.4}$$

where R_{ACT} is a formation rate of acetone, *k* is a rate constant, and P_{C} is the partial pressure of propane. An Elley–Rideal mechanism can postulate the following reaction scheme:

$$C_3H_8 + S \rightarrow C_3H_8 - S \tag{1}$$

$$C_3H_8 - S + O_2 \rightleftharpoons C_3H_6O - S + H_2O$$
(2)

$$C_3H_6O - S \rightleftharpoons C_3H_6O + S \tag{3}$$



Figure 3. Log-log plot for propane pressure and the formation rate of acetone in photooxidation of propane over Rb-VS.



Figure 4. Effect of oxygen pressure on the formation rate of acetone in photooxidation of propane over Rb-VS.



Figure 5. Effect of water pressure on the formation rate of acetone in photooxidation of propane over Rb-VS.

where S indicates the photocatalytic active site (VO₄Rb species) of Rb-VS. Under irradiation, the active sites are excited to the triplet state. Here, k_1 refers to a rate constant for propane adsorption on the active site (eq 1), K_2 is the equilibrium constant for the photooxygenation of pre-adsorbed propane with molecular oxygen (eq 2), and K_3 is the equilibrium constant for the desorption of photogenerated acetone (eq 3). The equilibrium process for propane adsorption was not taken into account since photoadsorbed propane is hardly desorbed from the active site even under evacuation; in other words, the adsorbed species has a strong chemical interaction with the active site.²⁹

The formation rate of propane was independent of oxygen pressure as shown in Figure 4. The 0th order against the oxygen pressure indicates that the rate-determining step is eq 1.

In the photooxidation of propane, water is generated by production of acetone and total oxidation to CO_2 . Figure 5 shows the effect of partial pressure of water on the formation rate of acetone. There was no hindrance by water vapor until the partial



Figure 6. FT-IR spectra of acetone species adsorbed on Rb-VS. After introduction of 1.0 Torr acetone at room temperature, the Rb-VS was evacuated at (a) room temperature, (b) 333 K, and (c) 423 K.

pressure reached the saturated humidity at 333 K. Water pressure can be excluded from the rate equation.

Assuming that eq 1 is the rate-determining step, the formation rate of acetone is given according to the following equation:

$$R_{\rm ACT} = k_1 P_{\rm C}[S] \tag{4}$$

$$[S] = \frac{[S_0]}{1 + (P_{ACT}/K_3)(1 + 1/K_2P_0)}$$
(5)

where P_{ACT} is the partial pressures of acetone, and [S] and [S₀] are the total number of active sites and the number of vacant sites, respectively. The numerical value of K_2 was expected to be large because the water vapor cannot affect the formation rate. If the numerical value of K_2P_0 was much larger than 1, the following equation is derived:

$$R_{\rm ACT} = k_1 P_{\rm C} \frac{[{\bf S}_0]}{1 + (P_{\rm ACT}/K_3)}$$
(6)

This equation represents the experimental results of 0th order against oxygen pressure at steady state as shown in Figure 4. Since acetone is strongly adsorbed on the surface of Rb-VS, the numerical value of K_3 is assumed to be small. Therefore, the term of P_{ACT} , which includes the contribution of P_C , is not negligible. The rate equation explains that the order against propane pressure was less than 1st, being consistent with experimental result.

The experimental data against the propane pressure (Figure 2) were well curve-fitted by the method of least squares using the rate equation, eq 6. Kinetic analysis gave the values as follows: $k_1 = 6.68 \times 10^3$ atom⁻¹ g-cat⁻¹ h⁻¹, $K_3 = 1.17 \times 10^{-6}$ atm⁻¹. The small numerical value of K_3 indicates that the equilibrium was inclined to the adsorption of photogenerated acetone on the active site.

Improvement of Photocatalytic Activity. Kinetic study suggested that the rate-determining step is the photoadsorption of propane. By increasing the number of the vacant sites [S₀], most of which are occupied by adsorbed acetone, the reaction rate will increase. Figure 6 shows FT-IR spectra of adsorbed acetone species on Rb-VS. The strong bands at 1700 and 1712 cm⁻¹ are attributed to the stretching vibration mode of C=O. The bands at 1424 and 1370 cm⁻¹ are the asymmetric and symmetric deformation mode of the methyl group, respectively. The acetone adsorbed on the catalyst surface remained even at 333 K evacuation (Figure 6b). This corresponds to the low value



Figure 7. Product yield in photoassisted oxidation of propane over Rb-VS at 333-473 K: \bullet acetone, \blacktriangle propionaldehyde, \bigcirc ethanal, \triangle CO₂, and \Box CO.

of K_3 in eq 6. Raising the evacuation temperature to 423 K, the adsorbed acetone was fully removed. So, heating the catalyst bed would enhance the formation rate of acetone in the photooxidation due to the promotion of the desorption of acetone from active sites.

We carried out the photoassisted oxidation of propane by molecular oxygen over Rb-VS at 333-473 K by heating the catalyst bed (Figure 7). This procedure increased the formation rate of acetone by two times, as theoretically expected. In addition, the propanal (propionaldehyde) yield increased greatly (that is a minor product at 333 K). By raising the temperature of the photocatalyst bed up to 473 K, the total yield of acetone and propionaldehyde reached three times higher values than those in the reaction at 333 K. Note that the yield of carbonyl compounds increased by raising the reaction temperature while that of CO₂ hardly changed in the photooxidation over Rb-VS. At temperatures lower than 623 K, there was no production in the dark reactions of propane with molecular oxygen over Rb-VS. Dark thermal conditions at temperatures more than 623 K merely promoted total oxidation to CO_X as the main product.

Discussion

We assumed that the photoadsorption of propane was the ratedetermining step, and the Elley-Rideal mechanism can explain the reaction rate. It was suggested that the occupation of the active site by photogenerated acetone suppressed the rate of photoadsorption of propane on Rb-VS. In fact, raising the photoreaction temperature enhanced the formation rate of acetone due to an increase of the vacant active sites. The high reaction temperature not only enhanced the product yield but also changed the product selectivity. The propionaldehyde yield increased with an increase in the photoreaction temperature.

We guess that acetone and propionaldehyde are formed through the attack of the hydrogen atom of secondary C-H and primary C-H of propane by active oxygen species, respectively. The result of photooxidation of propane over Rb-VS using ¹⁸O-labeled molecular oxygen shows that the ¹⁶Olabeled oxygenated product was generated at the initial stage.¹¹ This indicates that an active oxygen species is not derived from molecular oxygen but from lattice oxygen of the vanadium species. The semi-occupied nonbonding orbital of oxygen atoms interacting with an alkali cation, which is formed by the excitation from ground state to triplet state, is assumed to be the active site for interaction with HOMOs localized on C-H bonds of propane.²⁹ The stabilization energy for adsorption of propane on the lattice oxygen of a photoactivated VO₄K model cluster in the alkali-ion-modified VS has been estimated by means of ab-initio quantum-chemical calculations in the case



Figure 8. The proposed intermediates for the formation of (a) acetone and (b) propionaldehyde in photooxidation of propane over Rb-VS.

of the attack of the hydrogen atom of a secondary C–H bond and a primary C–H bond of propane, respectively.²⁹ The energy difference between propane adsorbed at the methylene group and the methyl group is calculated to be about 4.2 kJ mol⁻¹ (1.0 kcal mol⁻¹).

FT-IR study has suggested that the photoadsorbed propane species has a strong chemical interaction with Rb-VS, since the adsorbed species remain on Rb-VS after evacuation at room temperature.²⁹ By comparing the vibrational spectra of the photoadsorbed species with that of vanadyl triisopropoxide VO(O- iC_3H_7)₃, we have concluded the presence of an isopropoxide-like intermediate that is attached to the vanadium species with cleavage of a C–H bond of propane when propane adsorbs on the surface of Rb-VS under photoirradiation. This intermediate is assumed to be the precursor into acetone. In the same way, the precursor into propionaldehyde is assumed to be a *n*-propoxide-like intermediate. The proposed intermediates are shown in Figure 8, and eq 1 is rewritten as follows for a good understanding:

$$C_{3}H_{8} + S \rightarrow C_{3}H_{7} - V^{4+}O_{4}Rb + H^{+}$$
 (7)

Here, we guess that the formation mechanisms of acetone and propionaldehyde are the same and the selectivity is dominated by the difference between the stabilizing energy of the adsorbed intermediates. Provided that the formation ratio of acetone to propionaldehyde obeys Boltzmann's distribution of stabilizing energy difference, ΔE , between the precursor into acetone and the precursor into propionaldehyde, the ratio is expressed as follows:

$$\frac{R_{\rm ACT}}{R_{\rm PA}} = \exp\left(\frac{\Delta E}{RT}\right) \tag{8}$$

where R_{PA} is the formation rate of propionaldehyde, *R* is the gas constant, and *T* is the reaction temperature. Figure 9 shows the logarithm plots of the formation ratio of acetone to propionaldehyde (R_{ACT}/R_{PA}) against the reciprocal of the reaction temperature in photooxidation of propane over Rb-VS. A linear relationship suggested that the formation ratio of precursor-into-acetone to precursor-into-propionaldehyde obeys Boltzmann's distribution. The stabilizing energy difference between the precursors was estimated to be 11.4 kJ mol⁻¹ (2.7 kcal mol⁻¹) by a slope of Figure 9 ($\Delta E/R$).

We carried out the DFT calculations of total energy of 2-propanol and 1-propanol, which were briefly substituted as the isopropoxide-like intermediate and the *n*-propoxide-like intermediate, respectively. The stabilizing energy difference between 2-propanol and 1-propanol was 14.1 kJ mol⁻¹ (3.4 kcal mol⁻¹), as shown in Figure 10. This is nearly consistent with the result of the formation ratio of acetone to propionaldehyde ($\Delta E = 2.7$ kcal mol⁻¹). Therefore, it was clarified that the rate-determining step of photooxidation of light alkanes over Rb-VS was photoadsorption of alkanes to lattice oxygen of the



Figure 9. Logarithm plots of the formation ratio of acetone (ACT) to propionaldehyde (PA) against the reciprocal of the reaction temperature in photooxidation of propane over Rb-VS.



Figure 10. The energy difference between 2-propanol and 1-propanol (C = gray, O = black, H = small white spheres) calculated by B3LYP method.

active site, and the alkoxide intermediates were created for formation of ketones and aldehydes. In the case of photooxidation of propane, the ratio of isopropoxide-like intermediate to *n*-propoxide-like intermediate, which decides the ratio of acetone to propionaldehyde, obeys Boltzmannn's distribution of the energy difference.

Conclusions

To improve the photocatalytic activity of Rb-VS by optimization of the reaction conditions on the basis of the reaction scheme, we investigated the rate-determining step of the reaction path by kinetic analysis. The formation rates of acetone by changing the pressure of propane and oxygen were measured, and the rate expression was determined as follows:

$$R_{\rm ACT} = k P_{\rm C}^{0.4}$$

We assumed that the photoadsorption of propane on the active site is the rate-determining step, and the Elley-Rideal mechanism can explain the reaction rate. By increasing the number of the vacant sites $[S_0]$, most of which were occupied by photogenerated acetone during the reaction, the formation rate of acetone was expected to increase. When heat was applied to the reaction system, a great improvement of the photocatalytic activity was achieved. Moreover, the product selectivity, the ratio of acetone to propionaldehyde, was changed. The ratio was explained by Boltzmann's distribution of the difference of the stabilization energy of the intermediates (alkoxides bound to vanadium species). It was suggested that the isopropoxide-like and *n*-propoxide-like intermediates were formed as the precursors into acetone and propionaldehyde, respectively.

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