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Photocatalytic oxidation of alkane at a steady rate over alkali-ion-modified vanadium oxide supported on silica

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Abstract

Photocatalysts were applied to photocatalytic oxidation of propane in a fixed bed flow reactor. Titanium dioxide exhibited fairly high activity but the deep oxidation was predominant. Silica-supported vanadium oxide (VS) favors the partial oxidation to form propanone and variety of aldehydes and the fast deactivation took place accompanied by reduction of vanadium ions. On the other hand, alkali-ion-modified VS exhibited the highest activity and high selectivity to propanone. The activity was stable because vanadates in alkali-ion-modified VS do not change their structure or are not poisoned by water molecules throughout the reaction. The cleavage of C=C double bond to form aldehydes predominantly proceeded in the case of photo-oxidation of 1-butene over VS while in the case of photo-oxidation of Rb-modified VS, the oxidation of secondary carbon atom to form methyl vinyl ketone is favored. Methyl ethyl ketone was produced at a steady rate over Rb-VS in the photo-oxidation of *n*-butane. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalytic oxidation; Alkali-ion; Vanadium oxide

1. Introduction

Photocatalysis is of current interest from the view of the utilization of light energy. Photodecomposition of water and removal of pollutants in air and wastewater are the predominant themes. Titanium dioxide was once studied for the photo-oxidation of hydrocarbons and alcohols. At present, however, degradation of organic compounds over illuminated TiO_2 relating to environmental catalysis is widely studied and partly applied because of its strong oxidizing capability. Actually, oxidation of propene over illuminated TiO_2 is reported to give carbon dioxide as the main product even at a low level of conversion of propene (0.055%) [1]. Therefore, it is difficult to develop photocatalysis system as a selective oxidation of hydrocarbons with semiconductor catalysts. On the other hand, we have reported that photo-oxidation of alkenes over silica-supported vanadium oxide produces aldehydes and ketones mainly [2,3] and the catalyst is promising for partial oxidation of hydrocarbons. Not only alkenes but also alkanes are oxidized to partial oxidation products over illuminated silica-supported vanadium oxide although various aldehydes and ketones are formed [4].

Previously we have reported that modification of silica-supported vanadium oxide by addition of alkali ions results in improvement of selectivity for photocatalytic oxidation of alkene [4] and alkane [5,6] as well as enhancement of activity [4] confirmed with an integrated reactor. In the presence

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of water molecules V_2O_5/SiO_2 (VS) changes its structure of an active site by adsorption of water molecules [7] while alkali-ion-modified catalyst does not [8], suggesting the less deactivation of the alkali-ion-modified catalyst. These properties led us expect that alkali-ion-modified vanadium oxide supported on silica can be utilized as a catalyst in a flow reactor and in a practical use. Furthermore, the modified catalyst has another remarkable property that it works under visible light illumination [5,6,9].

In the present paper, we report that the catalysis system of selective photo-oxidation of propane with alkali-ion-modified vanadium oxide supported on silica can be operated without deactivation at a high rate of production of acetone and discuss the characteristics of the reaction system.

2. Experimental

2.1. Materials and sample preparation

Silica was prepared by the hydrolysis of the distilled tetraethyl orthosilicate (TEOS) commercially supplied, followed by calcination in dry air stream at 773 K for 5 h as described elsewhere [10]. VS was prepared by impregnating SiO_2 with an aqueous solution of ammonium metavanadate in the same manner in Ref. [10]. The loading amount of vanadium ions was 2.5 wt.% as V_2O_5. The alkali-ion-modified catalyst was prepared by impregnation of VS with an aqueous solution of alkali metal hydroxide, followed by calcination with a dry air stream at 773 K for 5 h. Na-, K- and Rb-added VS are denoted as Na-VS, K-VS and Rb-VS and amount of alkali ion was adjusted to be alkali/V=1.5 except for otherwise noted. Molybdenum containing samples were prepared in the same manner with ammonium heptamolybdate instead of ammonium metavanadate as vanadium containing samples. TiO_2 (P25, Degussa) was commercially supplied.

2.2. Reaction procedure

Three hundred milligrams of the catalyst was diluted with 4.5 g of quartz powder and mounted on a catalyst bed made of Pyrex glass (volume, $3\,cm^2$). The pretreatment of the catalyst was carried out by heating at 673 K under the atmospheric stream of helium and oxygen (80:20) mixture at a flow rate of 100 ml/min. The authentic reaction was carried out under a total flow rate of 100 ml/min of a gas mixture of propane, oxygen and helium (20:10:70) controlled by mass-flow controllers at an atmospheric pressure. The products were analyzed by gas chromatographs connected directly with a flow reactor. A 300 W high pressure xenon lamp was used as the light source with glass filters, UV31 and UV39 which can permit ultraviolet and visible (UV/Vis) lights with $\lambda>310$ and 390 nm, respectively. The temperature of the catalyst bed was 323 K. Product selectivity was calculated on the basis of the product yield normalized to the reciprocal of number of carbon atoms included in the product molecule.

2.3. Characterization of catalyst samples

Diffuse reflectance UV/Vis spectra were recorded with a Perkin-Elmer lambda 19 spectrometer equipped with integration spheres and the sample was manipulated without exposure to the air. Powder X-ray diffraction (XRD) patterns were collected with a Rigaku Geiger-flex 2015 diffractometer with Ni-filtered Cu Kα irradiation.

3. Results

3.1. Propane photo-oxidation over vanadium oxide catalysts

Fig. 1 showed the time course of products yield in photo-oxidation of propane over VS irradiated through a UV-31 filter. The various oxidation products, CH_3CHO, C_2H_5CHO and $(CH_3)_2CO$, were formed at production rates of 0.5–0.6 μmol/min at an initial stage and after 60 min operation, the production rates were reduced to 60%. Throughout the reaction, only a trace amount of CO_x was detected. The color of VS changed from faintly yellow to dark purple with reaction time indicating that deactivation of the catalyst may be accompanied by the reduction of vanadium cations. When the UV39 filter was used, the propane was not converted at all. VS is UV-ray active. On the other hand, in case of Rb-VS, $(CH_3)_2CO$ was selectively produced at a steady rate

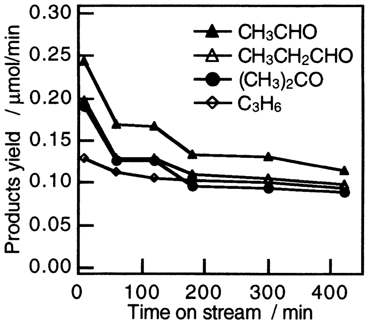

Fig. 1. Time course of photo-oxidation of propane over V_2O_5/SiO_2 (VS) under irradiation for λ>310 nm.

(1.4 µmol/min) after 30 min time on stream as shown in Fig. 2. Although the rate of total oxidation is higher than that found in the case of VS, the formation rate of propanone is much higher. When the UV39 filter was used, the production rate decreased probably because of the reduction of photon-flux as shown in Fig. 3. Propanone was formed at a rate of 0.4 µmol/min and selectivity to total oxidation decreased remarkably. During the reactions, the color of the catalyst did not change. This shows that the reduction of vanadium cations or deactivation of the catalyst by adsorption of water molecules did not occur.

3.2. Propane photo-oxidation over various photocatalysts

The performance of other photocatalysts, Mo/SiO_2 [11,12], $RbMo/SiO_2$ [11,12] and TiO_2 were examined together with vanadium oxide catalysts. The photo-oxidation results obtained at 60 min irradiation time through a UV-31 filter are summarized in Table 1. The silica-supported molybdenum oxide catalysts exhibited very poor activity, although the selectivity to propanone became fairly high for alkali-ion-modified. The phenomenon of the improvement of the selectivity by addition of alkali ions is the same as observed in the case of vanadium containing catalyst. TiO_2 showed fairly high activity because catalyst amount was very high. The selectivity to propanone over TiO_2 is appreciably high but total oxidation is predominant. The selectivity of alkali-ion-modified VS catalysts is similar to each other and the activity of Rb-VS is the highest among the examined catalyst samples. Table 2 shows the results of photo-oxidation with a UV-39 filter. Evidently, VS, molybdenum-containing catalysts and TiO_2 are inactive against visible light irradiation. The conversion of propane over alkali-ion-modified VS catalysts is reduced by cutting off the UV-ray but the catalysts still exhibited stable activity. As mentioned above, alkali-ion-added VS catalysts exhibited the highest activity and the order of the activity is Rb>K>Na, which was the same as found in our earlier work [5,6].

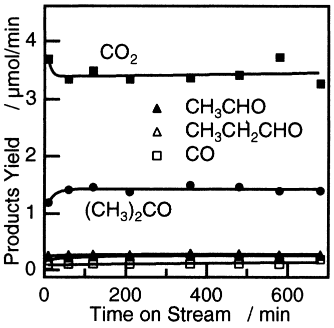

Fig. 2. Time course of photo-oxidation of propane over $Rb-V_2O_5/SiO_2$ (Rb-VS) under irradiation for λ>310 nm.

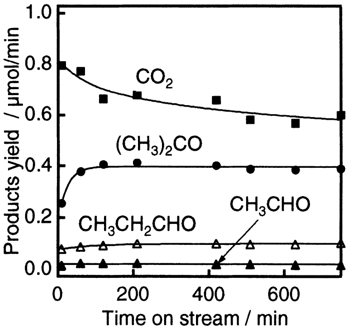

Fig. 3. Time course of photo-oxidation of propane over Rb-VS under irradiation for λ>390 nm.

3.3. The effect of partial pressure of propane and oxygen on photo-oxidation over Rb-VS

Under the condition that the total flow rate (100 ml/min) and partial pressure of propane (152 Torr) were fixed, the reaction was carried out changing the partial pressure of oxygen. The results are shown in Fig. 4. The production rates were found

Table 1
Conversion and selectivity in percent for photo-oxidation of propane over various photocatalysts (λ>310)[a]

Catalyst	Conversion (%)	C_3H_6	CH_3CHO	C_2H_5CHO	$(CH_3)_2CO$	Co_x
VS	0.11	9	36	27	287	Trace
Rb-VS	0.47	Trace	8	6	43	42
K-VS	0.31	Trace	6	5	45	43
Na-VS	0.24	Trace	11	12	44	33
Mo/SiO_2	0.01	42	29	11	17	Trace
$RbMo/SiO_2$	0.02	Trace	Trace	11	88	Trace
TiO_2	0.42	0	Trace	Trace	31	68

[a] The data were obtained at 60 min time on stream.

Table 2
Conversion and selectivity in percent for photo-oxidation of propane over various photocatalysts (λ>390)[a]

Catalyst	Conversion (%)	C_3H_6	CH_3CHO	C_2H_5CHO	$(CH_3)_2CO$	Co_x
VS	Trace	–	–	–	–	–
Rb-VS	0.09	Trace	3	11	51	33
K-VS	0.09	Trace	3	10	60	26
Na-VS	0.06	–	4	19	57	20
Mo/SiO_2	0	–	–	–	–	–
$RbMo/SiO_2$	Trace	–	–	–	–	–
TiO_2	0	–	–	–	–	–

[a] The data were obtained at 60 min time on stream.

to be almost constant to the partial pressure of oxygen except for the formation rate of carbon dioxide, which decreases in the region of high partial pressure of oxygen. Total oxidation on Rb-VS is suppressed by excess oxygen. Fig. 5 shows the results of the reactions carried out under the condition that the total flow rate and partial pressure of oxygen (152 Torr) were fixed, changing the partial pressure of propane from 75 to 450 Torr. The propanone yield increased with increasing the partial pressure of propane and the formation rate of carbon dioxide did not changed at higher propane pressures than 152 Torr. It results in the great enhancement of the selectivity to propanone up to 55%. This indicates that the mechanisms for partial oxidation and total oxidation are different from each other.

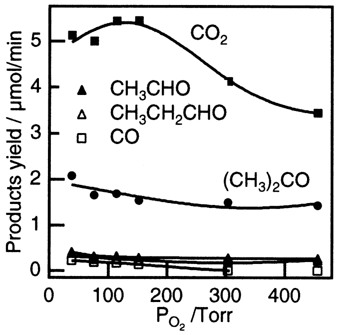

Fig. 4. Change in the products yield with partial pressure of oxygen in photo-oxidation of propane over Rb-VS. $P(C_3H_8)$=152 Torr.

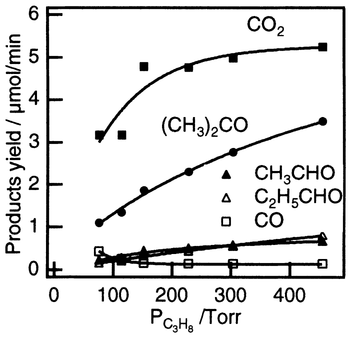

Fig. 5. Change in the products yield with partial pressure of propane in photo-oxidation of propane over Rb-VS. $P(O_2)$= 152 Torr.

4. Discussion

4.1. Catalyst deactivation of VS and visible light response of Rb-VS

The deactivation of VS as shown in Fig. 1 was suggested to be due to the reduction of vanadium ions judging from the color change of the catalyst during the reaction whereas Rb-VS exhibited stable activity. The other reason for the deactivation of VS is considered to be due to the adsorbed water molecules formed during the reaction blocking the active sites. We have previously reported that vanadium ions over silica coordinate water molecules tightly at low temperature [7,13], while water molecules are not coordinated to vanadium ions in Rb-VS [8]. To examine whether reduction of vanadium ions or occupation of active sites brought about the deactivation by water molecules, we carried out the measurement of UV/Vis spectra. Fig. 6 shows the UV/Vis spectra of VS and Rb-VS. The spectrum of VS before reaction exhibits sharp absorption edge at less than 400 nm suggesting that VS is Vis-inactive. Fig. 6 also shows the spectra of hydrated VS samples. Adsorption of water molecules on VS results in the formation of absorption band toward longer wavelength than the absorption edge proving the dark yellow color of the fully hydrated sample. In case of VS after reaction for 6 h, the spectrum exhibits another absorption band tailing toward 800 nm assignable to d–d transition of V^{4+} ions and evidently the band due to adsorption of water molecules is missing. The result clearly shows that the deactivation of VS was caused by the reduction of vanadium ions. In case of Rb-VS, the spectra of unused and used samples are almost identical with each other except for a slight discrepancy in the region of low wavelength. This shows that the state of Rb-VS does not change after the reaction and this explains why Rb-VS exhibits stable activity. The spectrum of Rb-VS exhibits absorption edge at longer wavelength than that found in the case of VS. To clarify the difference in UV/Vis spectra of VS and Rb-VS, the spectra were expanded in the range around absorption edges. The expanded spectra are shown in Fig. 7 and the difference between absorption edges is clearly seen. The addition of Rb ions to VS causes the structural change of vanadate species [4,8,14], which lowers the excitation energy of the charge transfer between vanadium and oxygen atoms [8,15]. Fig. 7 shows the action spectrum of propanone yield in the photo-oxidation of propane with monochromatized lights normalized to photon flux. The photoefficiency was estimated assuming that the formation of one molecule of propanone requires one photon. The shape of the action spectrum is consistent with the discrepancy between spectra of Rb-VS and VS. This means that the exciton is localized on the specific bond and is different from that formed in/on semiconductor materials like titania. The photoefficiency at 390 nm was evaluated to be 0.11 and this is well consistent with our previous report [8]. Photoefficiency is apparently the quantum yield and should be regarded as the lowest value in view of the loss of the light intensity due to scattering by the catalyst. Therefore, the photoefficiency is not low in the present system.

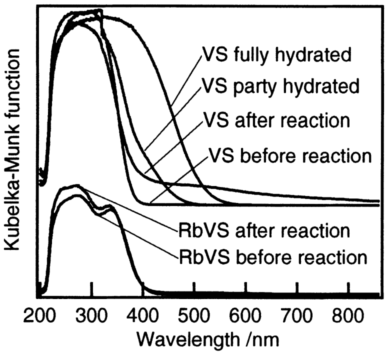

Fig. 6. Diffuse reflectance UV/Vis spectra of VS and Rb-VS.

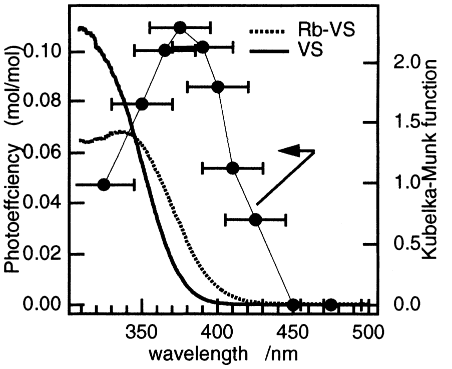

Fig. 7. Diffuse reflectance UV/Vis spectra of VS and Rb-VS and action spectrum on the propanone yield.

Table 3
Conversion and selectivity in percent in photo-oxidation of *n*-butane over VS and Rb-VS[a]

Catalyst	UV filter[b]	Conversion (%)	CH_3CHO	C_2H_5CHO	C_3H_7CHO	$CH_3COC_2H_5$	Co_x
VS	31	0.05	49	8	27	15	Trace
Rb-VS	31	0.56	19	7	7	44	23
Rb-VS	39	0.15	11	5	11	58	14

[a] The data were obtained at 5 h time on stream.
[b] Glass filters, UV-31 and UV-39, see text.

4.2. Reaction mechanism

The reaction mechanism of photo-oxidation of propane was already reported in the previous report [15]. Propane is adsorbed very fast upon irradiated catalyst and immediately changes to isopropoxide on the surface. Oxygen molecules are adsorbed on irradiated catalyst having adsorbed propane to form propane–oxygen complex. The adsorbed form of propane and isopropoxide species determines the selectivity to propanone. Therefore, secondary or tertiary carbon atom of the alkane is attacked over alkali-ion-modified VS. The activity of alkene photo-oxidation over the alkali-ion-modified catalyst is lower than that of alkane [16] since alkenes are photoadsorbed on VS catalyst electron-donatively [17] and the existence of alkali ions increases electron population in surface vanadate species making it difficult to withdraw an electron from alkene [18]. Taking into account the property of alkali-ion-modified VS, it is expected that photo-oxidation of 1-butene produces but-3-en-2-one (methyl vinyl ketone). In case of VS, main product of photo-oxidation of VS is propanal formed by the cleavage of C=C double bond [3]. We carried out photo-oxidation of 1-butene over Rb-VS in closed circulating system and confirmed that main product is methyl vinyl ketone, the yield of which is 10 times higher than that of propanal and other C_3 compounds. In the photo-oxidation of hydrocarbon over alkali-ion-modified VS, the oxidation of secondary carbon is favored rather than the cleavage of C=C double bond and C–C bond. Thereby the replacement of propane with *n*-butane as a reactant allows us to expect the formation of 2-butanone (methyl ethyl ketone). Table 3 shows the results of photo-oxidation of *n*-butane over VS and Rb-VS catalysts at 5 h time on stream. The reaction condition is the same with that for propane oxidation. The activity of VS was lower in the present case than that for propane oxidation and VS is inactive against visible light irradiation. On the contrary, Rb-VS exhibits higher activity than that for propane oxidation. The activity was reduced by cutting off UV light but still stable activity existed. The main product is methyl ethyl ketone as expected.

5. Conclusion

Alkali-ion-modified VS catalysts are effective for photo-oxidation of alkane to form a ketone selectively at a steady rate at low temperature. Solar energy is available as a light source. The reaction selectivity is very intriguing that oxidation of secondary carbon is favored rather than the cleavage of C–C bond and deep oxidation. In case of photo-oxidation of propane, space time yield (STY) of propanone is 2.8 mmol/(h l) using 300 W Xe lamp as a light source. Although the conversion is still low, the result reported here suggests that the photocatalytic oxidation is no longer at the level of fundamental work in the laboratory. The mild reactions condition of ambient pressure, low temperature, high formation yield and high selectivity lead us to expect that photocatalysis will play a significant role in the future.

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