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Selective Photooxidation of Propane to Propanone over Alkali-ion-modified Silica-supported Vanadium Oxides

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The addition of alkali ions (Na, K and Rb) to silica-supported vanadium oxide results in the formation of surface vanadate species which is excited by the light with wavelengths of around 400 nm. Propanone was selectively formed from propane and oxygen over alkali-ion-modified silica-supported vanadium oxides by the photoirradiation of light with wavelengths of $\lambda > 390$ nm.

Selective conversion of light alkanes to other valuable compounds is of current interest and many efforts have been made to improve the efficiency in this area.[1)] Furthermore, the selective oxidation of light alkanes has been one of the main themes in heterogeneous photocatalysis.[2)] However, except for the selective formation of ketones from isoalkanes accompanied by C-C bond fissions by photocatalysis over TiO_2[3b)] and the selective conversion of methane to formaldehyde over photoirradiated MoO_3/SiO_2 at 493 K,[3c)] the reaction is not usually selective.[3a)] The reason is thought to be that the consecutive oxidation of partial oxidation products and/or intermediates takes place easily or that C-C activation is preferential to C-H activation on photocatalysts.

In the present paper, we wish to report the formation of highly photoactive surface vanadate species on alkali-ion-modified V_2O_5/SiO_2 which is photoexcited by around 400 nm light and selective conversion of propane to propanone over the catalyst under photoirradiation with wavelengths of $\lambda > 390$ nm at room temperature.

The V_2O_5(2.5 wt%)/SiO_2(VS) was prepared by an impregnation method reported previously.[4)] The alkali-ion-modified catalysts were prepared by impregnation of VS with aqueous solutions of NaOH, KOH and RbOH, followed by calcination at 773 K in a stream of dried air. The contents of sodium, potassium and rubidium were 1, 2 and 4 wt% as Na_2O, K_2O and Rb_2O, respectively. Prior to reactions and measurements, the catalysts were evacuated for 1 h at 673 K and treated at 673 K under an O_2 atmosphere of 6.7 kPa for 2 h, followed by evacuation at 673 K for 10 min to condition the surface state. The reaction was carried out with a conventional gas-circulating system (dead space: 280 cm^3) with a quartz reactor,[5)] and a 250 W super high pressure Hg lamp was used as a light source. Irradiation was performed through glass filters, UV31 and UV39, permitting lights with wavelengths of $\lambda > 310$ nm and $\lambda > 390$ nm, respectively. The catalysts were irradiated for 1 h under an atmosphere of propane and oxygen and the products were analyzed by *g.l.c.* No products were formed without catalysts or irradiation. Photoluminescent emission spectra were recorded using a Hitachi F3010 spectrometer at 77 K.

Figure 1 shows the phosphorescent emission spectra of VS, Na_2O-VS, K_2O-VS and Rb_2O-VS excited by light with a wavelength of 310 nm. VS exhibits a characteristic spectrum with a fine structure due to the vibration of V=O bonds.[5-7)] The addition of alkali ions causes the fine structure to become vague and a different

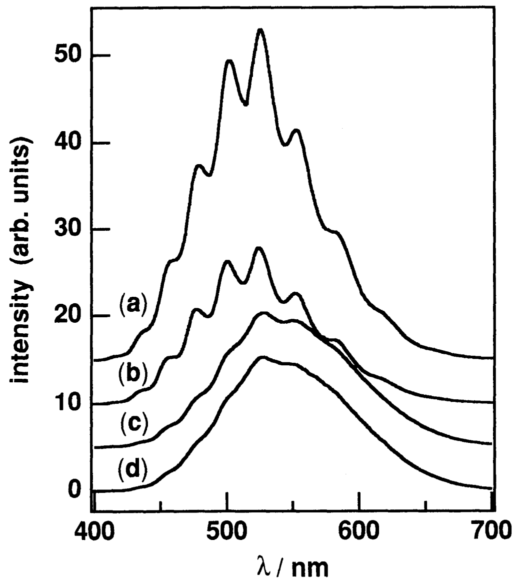

Fig. 1. Photoluminescent emission spectra at 77 K of (a) VS, (b) Na_2O-VS, (c) K_2O-VS and (d) Rb_2O-VS excited by light at 310 nm light. VS, see text.

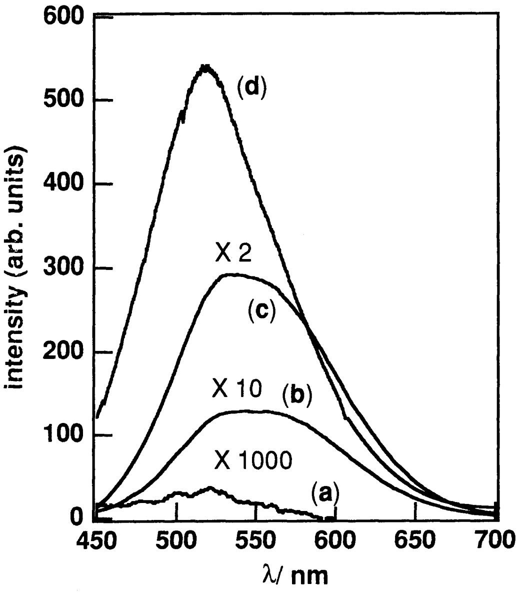

Fig. 2. Photoluminescent emission spectra at 77 K of VS and alkali-ion-added VS catalysts excited by 400 nm light. For (a) - (c), magnified intensity is shown. (a) - (d), see the caption to Fig. 1.

emission band can be observed as a shoulder in the vicinity of 530 nm. In particular, for Rb_2O-VS, a band at 530 nm can clearly be seen. Thus, there can be said to be two kinds of luminescent centers on alkali-ion-modified VS. To discriminate these emission bands, the excitation wavelength was changed. Figure 2 shows the emission spectra of the catalysts excited by 400 nm light. The intensity of the band becomes larger and the emission peak shifts to a shorter wavelength in the order of the atomic numbers of the added alkali ions. VS exhibits no emission when excited by 400 nm light. This clearly shows the presence of two kinds of photoemission sites on alkali-ion-modified catalysts. One, excited by light at around 310 nm is assigned to VO_4 ions on silica as reported by other groups[5-7] and the other which is excited by light at around 400 nm can tentatively be referred to as site-400. We have already concluded from EXAFS/XANES analysis[8] that isolated VO_4 interacting with sodium ions[9] is preferentially formed by the addition of sodium ions to VS and have reported that photocatalytic activity increased with an increase in the amount of the VO_4 species.[10] If this photoactive VO_4 is identical to site-400, its property as a photocatalytic site is intriguing. Table 1 shows the results of the reactions. When a UV-31 filter was used where both VO_4 on VS and a site-400 could be activated, the activity for alkali-ion-modified catalysts was much higher than for VS. On the other hand, the yield of partial oxidation products over Na_2O-VS, K_2O-VS and Rb_2O-VS were lower than that over VS. This indicates that total oxidation proceeds easily over alkali-ion-modified VS. However, the distribution of products by partial oxidation over VS scattered to many compounds while propanone was selectively formed over Na_2O-VS, K_2O-VS and Rb_2O-VS. In the absence of oxygen, activity was suppressed to low

Table 1. Photooxidation of propane over VS and alkali-ion-modified VS[a]

Catalyst[b]	Condition[c]	Conversion[d]	Selectivity[e] / %						
		/ %	C_3H_6	C_2H_5CHO	$(CH_3)_2CO$	$CH_2=CHCHO$	C_2H_4	CH_3CHO	COx
VS	UV31,A	63.4	10	12	16	1	2	17	42
Na_2O-VS	UV31,A	83.8	4	1	33	0	4	2	56
K_2O-VS	UV31,A	85.2	2	1	37	0	1	1	57
Rb_2O-VS	UV31,A	88.5	1	0	33	0	1	1	63
VS	UV31,B	11.6	80	0	4	0	6	5	5
Na_2O-VS	UV31,B	15.9	80	0	4	0	3	0	13
K_2O-VS	UV31,B	15.9	91	0	2	0	1	0	6
Rb_2O-VS	UV31,B	17.8	82	0	1	0	1	0	16
VS	UV39,A	5.0	43	19	15	0	tr	13	9
Na_2O-VS	UV39,A	60.3	8	7	52	0	1	7	25
K_2O-VS	UV39,A	67.0	4	2	51	0	1	3	39
Rb_2O-VS	UV39,A	67.1	3	1	60	0	1	1	34

a) Catalyst 0.5 g, irradiation time 1 h, reaction temperature at 308 K. b) VS stands for V_2O_5/SiO_2. c) UV31 and UV39 are glass filters used for irradiation. A stands for the initial condition; propane 70 μmol and oxygen 70 μmol. B stands for the condition; propane 70 μmol in the absence of oxygen. d) Based on introduced propane. e) Based on converted propane.

conversion levels and product distribution was quite different from that found in the presence of oxygen. After irradiation, all the catalysts changed from white to dark colour, indicating that the photoreduction of vanadium ions occurred. Propene was a predominant product over all the catalysts although some amounts of ethanal and ethene were formed over VS. This suggests that the oxidation mechanism is different from that involved in the presence of oxygen. One conjecture may be that propene is an intermediate in the reaction in the presence of oxygen as proposed by Djeghri and Teichner[3b] in the case of photocatalysis by TiO_2. However, we have already reported[10] that the main products in the photooxidation of propene over Na_2O-VS are acraldehyde and ethanal and that no formation of propanone, a main product in the photooxidation of propane, was observed.

When the reactions were carried out with a UV-39 filter, VS was for the most part inactive. The effective wavelengths to activate the VS catalyst are in the region of 310 - 380 nm, as has been reported previously.[5-7,11] The photoactive surface species on VS are only those emitting phosphorescence with a fine structure as shown in Fig. 1. On the other hand, alkali-ion-modified VS exhibited fair activity by irradiation through UV-39, which can be attributed to the presence of the site-400. Yields of partial oxidation products were higher than those in the case of the reaction with the UV-31 filter, indicating that capacity for the partial oxidation of propane was retained and total oxidation to CO_2 and CO was suppressed. It should be noted that the selectivity to propanone was very high in the order of Rb > K > Na. This is the same order as was found in the intensity of the emission spectrum excited by 400 nm light depicted in Fig. 2. From these results, we have concluded that the addition of alkali-ions results in the formation of another type of surface active vanadate species which can be excited by light at around 400 nm and shows a high activity to oxidize propane without C-C bond fissions in the presence of oxygen. In the present catalysts, almost all equimolar alkali ions and vanadium ions were contained but we found that the surface species, site-400 is not an alkali vanadate such as

$NaVO_3$ or Na_3VO_4.[10] The structural and electronic analysis of site-400 is now in progress.

References

1) J. R. H. Ross, R. H. H. Smits, and K. Seshan, *Catal. Today*, **16**, 503 (1993); A. Corma, J. M. López Nieto, and N. Paredes, *J. Catal.*, **144**, 425 (1993); G. Giannetto, A. Montes, N. S. Gnep, A. Florentino, P. Cartraud, and M. Guisnet, *ibid.*, **145**, 86 (1993); H. Igarashi, K. Tsuji, T. Okuhara, and M. Misono, *J. Phys. Chem.*, **97**, 7065 (1993); M. C. Kung and H. H. Kung, *J. Catal.*, **134**, 668 (1992); D. S. H. Sam, V. Sönen, and J. C. Volta, *ibid.*, **123**, 417 (1990).

2) R. I. Bickley, "Catalysis. Specialist Periodical Report," ed by G. C. Bond and G. Webb, The Chemical Society, London (1982), Vol. 5, p. 308; M. Formenti and S. J. Teichner, "Catalysis. Specialist Periodical Report," ed by G. C. Bond and G. Webb, The Chemical Society, London (1978) Vol. 2, p. 87.

3) a)D. L. Nguyen, P. C. Roberge, and S. L. Kaliaguine, *Canad. J. Chem. Eng.*, **57**, 288 (1979); S. L. Kaliaguine, M. Gnakoury, and P. C. Roberge, *Canad. J. Chem. Eng.*, **59**, 710 (1981); S. L. Kaliaguine, B. N. Shelimov, and V. B. Kazansky, *J. Catal.*, **55**, 384 (1978); K. Marcinkowska, S. L. Kaliaguine, and P. C. Roberge, *ibid.*, **90**, 4 (1984); b)N. Djeghri and S. J. Teichner, *ibid.*, **62**, 99 (1980) ; c) K. Wada, K. Yoshida, Y. Watanabe, and T. Suzuki, *J. Chem. Soc., Chem. Commun.*, **1991**, 726.

4) S. Yoshida, T. Matsuzaki, T. Kashiwazaki, K. Mori, and K. Tarama, *Bull. Chem. Soc. Jpn.*, **47**, 1564 (1974).

5) S. Yoshida, T. Tanaka, M. Okada, and T. Funabiki, *J. Chem. Soc., Faraday Trans. 1*, **80**, 119 (1984).

6) A. M. Gritscov, V. A. Shvets, and V. B. Kazansky, *Chem. Phys. Lett.*, **35**, 511 (1975).

7) M. Anpo, I. Tanahashi, and Y. Kubokawa, *J. Phys. Chem.*, **84**, 3440 (1980); M. Anpo and Y. Kubokawa, *Rev. Chem. Intermed.*, **8**, 105 (1987) and references therein.

8) T. Tanaka,Y. Nishimura, S. Kawasaki, T. Funabiki, and S. Yoshida, *J. Chem. Soc., Chem. Commun.*, **1987**, 506.

9) Y. Nishimura and S. Yoshida, "Computer Aided Innovation of New Materials II ," ed by M. Doyama, J. Kihara, M. Tanaka, and R. Yamamoto, Elsevier, Amsterdam (1993), p.1029.

10) T. Tanaka,Y. Nishimura, S. Kawasaki, M. Ooe, T. Funabiki, and S. Yoshida, *J. Catal.*, **118**, 327 (1989).

11) S. Yoshida, Y. Matsumura, S. Noda, and T. Funabiki, *J. Chem. Soc., Faraday Trans. 1*, **77**, 2237 (1981).

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