Selective photo-assisted catalytic oxidation of methane and ethane to oxygenates using supported vanadium oxide catalysts

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Selective photooxidation of light alkanes, mainly methane and ethane, into the corresponding aldehydes was achieved using silica-supported vanadium oxide catalysts under UV irradiation at elevated temperature. Photooxidation of methane using the V_2O_5/SiO_2-IW (incipient wetness) (0.6 mol% V) catalyst at 493 K for 2 h gave 68 μmol of methanal, which corresponds to 76 mol% selectivity and 0.48 mol% one-pass yield. Photooxidation of ethane using V_2O_5/SiO_2 (calcined at 1023 K) -IW (0.6 mol% V) catalyst for 1 h gave 85 μmol of ethanal, which corresponds to 90% selectivity and 1.1% one-pass yield. The catalysts prepared by the sol–gel method also showed activity, especially for the reaction of ethane. Both UV irradiation and a reaction temperature as high as 500 K were essential. The photo-assisted catalytic reactions were very sensitive to the reaction temperature, method of preparation of the catalyst, and addition of water vapour. While the reaction of methane was inhibited by the addition of water vapour, the photooxidation of ethane and propane was promoted in the presence of a controlled amount of water vapour. In addition, the reaction with methane required UV irradiation at a wavelength <310 nm, whereas the reaction with ethane or propane proceeded by irradiation at longer wavelength. According to Raman and UV diffuse reflectance spectroscopic studies and XRD studies, only isolated four-coordinated vanadium oxide surface species were considered to show catalytic activity toward the photooxidation of methane, while accumulated vanadium surface species, not crystalline V_2O_5, were shown to be active for the photooxidation of ethane and propane.

The development of the direct transformation of light alkanes into more valuable compounds with high conversions and selectivities is desirable.[1–3] However, there have only been a few successful attempts. In particular, the most expected selective aerobic oxidation of methane to oxygen-containing chemicals is still extremely difficult, in spite of recent interesting organometallic approaches.[2,3] As a method to overcome these barriers, the reaction of methane with N_2O in the presence of supported molybdenum oxide catalysts has been studied.[4] Selective formation of methanol was reported. The O^- radical anion on the surface was proposed to be the active and selective species. The results suggest that, if certain oxygen species can be produced on the surface of the catalyst, then selective oxidation could be achieved, even in the presence of dioxygen. In order to produce such oxygen species, the effect of UV irradiation of the surface of various metal oxide catalysts has been examined over the last two decades. The activities of both supported metal oxide catalysts and n-type solid oxide semiconductors towards photo-assisted catalytic oxidation of light alkanes have been examined.[5–13] These studies were mainly performed at ambient or lower temperature. Kaliaguine *et al.*[5] reported the reaction of methane and ethane by the use of γ-irradiation of metal complexes supported on silica; the major products were carbon oxides, together with a small amount of methanal. Ward *et al.*[6] reported the photooxidation of methane using silica-supported MoO_3 or $CuMoO_4$ catalysts at 313–373 K to give a small amount of methanol without deep oxidation, but the formation of methanal was not confirmed.

In these earlier studies, secondary deep oxidation of the adsorbed intermediates or products was considered to be mainly responsible for their low selectivities. In addition, irradiation of the surface of certain metal oxides was reported to induce spontaneous formation of various kinds of active oxygen species, which essentially decrease the selectivity. Differences in the thermal stabilities of active oxygen species have been reported.[14] For example, O^- radical anion species on silica-supported vanadium oxide, produced by the decomposition of adsorbed N_2O or O_2, were reported to be relatively stable, even above 500 K, whereas $O_2{}^-$ species were shown to have a shorter lifetime. Since desorption of reaction products from the surface is promoted at high temperatures, we examined the photooxidation of light alkanes at elevated reaction temperature. Successful results for the selective oxidation of methane, ethane and propane were obtained using silica-supported molybdenum oxide catalysts[15–17] or an n-type solid metal oxide semiconductor[18,19] at *ca.* 500 K. In these studies using silica-supported catalysts, we used a fluidized catalyst bed, in order to keep the temperature of the whole catalyst bed uniform, and to irradiate all particles of the catalyst. The reactions selectively yielded the corresponding aldehydes, but the conversions of methane did not reach the desired levels. In our preliminary account, the supported vanadium oxide catalysts were found to show excellent activity, especially for the reaction of methane.[20]

In the present paper our efforts were mainly focused on the design of optimum catalysts for the photooxidation of methane. The effects of the method of preparation was examined, in order to investigate the correlation between the activity and the surface state of the catalyst. The effects of reaction conditions, catalyst pretreatment and irradiation wavelength were also investigated.

Experimental

Materials

Silica-supported vanadium oxide catalysts were prepared by several methods: incipient wetness, designated V_2O_5/SiO_2-IW, evaporation to dryness (V_2O_5/SiO_2-ED), and sol–gel (V_2O_5/SiO_2-SG). To prepare the IW-catalysts, 5 g of silica gel (Alfa, BET surface area 260 m^2 g^{-1}, mean particle size 10 μm) was impregnated overnight in an oxalic acid solution of ammonium metavanadate (10 cm^3), followed by vacuum evaporation at 323 K and calcination in air at 823 K for 2 h.

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The V_2O_5/SiO_2-ED catalysts were prepared similarly, using 30 cm^3 of the solution. The V_2O_5/SiO_2-SG catalysts were prepared as follows: tetraethoxysilane (*e.g.* 49 mmol) in ethanol (5 cm^3) was mixed with vanadium oxyacetylacetonate (*e.g.* 1 mmol), dimethyl formamide (50 mmol), and water (10 cm^3). After gelation, the catalysts was dried and then calcined in air at 823 K for 2 h. The amount of vanadium in the catalyst after calcination was measured by atomic absorption and X-ray fluorescence analyses. The catalyst mounted in the reaction tube was again subjected to *in situ* calcination in a stream of air at 823 K for 2 h.

Highly purified methane (>99.9%, including less than 0.01% of ethane) was used without further purification. The as-supplied ethane, containing a small amount of CO_2 and water vapour, was slowly passed over a column filled with pulverized fused potassium hydroxide and molecular sieve 5A, and then fed to the reactor. Helium, propane, and oxygen were used as received. Other organic reagents were obtained from Wako Co., Ltd., and distilled just before use.

Apparatus and procedures

The reaction was carried out using an upstream flow-type reactor equipped with a preheater and a window for UV irradiation (10 mm × 20 mm, inner thickness: 1.0 mm) as described previously.[16] A quartz glass tube was fitted over the whole reactor in order to maintain the temperature of the catalyst bed uniformly by passing heated air around the reactor. The temperature of the irradiated surface of the catalyst was monitored by a thermocouple inserted directly into the catalyst bed. We confirmed the absence of the influence of this thermocouple on the yields of the products. There were only small variations in the temperature between the top and the bottom of the catalyst bed (*ca.* 15 K). UV irradiation was carried out with a high-pressure mercury vapour lamp (200 W, arc length; 75 mm) with a water filter. Chemical actinometry using iron(III) oxalate revealed that the number of photons irradiated to the catalyst bed was 3.3×10^{-7} einstein s^{-1} for 250–500 nm, 0.9×10^{-7} einstein s^{-1} for 250–300 nm, for both V_2O_5/SiO_2-IW and SG catalysts (0.025 g). Typical reaction conditions were: amount of catalyst, 0.025 g; feed rate of alkane, 7.5 mmol h^{-1} (180 cm^3 h^{-1}); alkane : oxygen : helium = 3 : 1 : 10 in molar ratio; W/F, 0.71 g h mol^{-1} (3.0×10^{-5} g h cm^{-3}). Liquid products were collected by passing through an ice–water trap at 273 K for the products of oxidation of methane, an acetone trap at 195 K for those from ethane and a methanol trap at 195 K for those from propane. Gaseous products were collected into gas-sampling bags.

Analysis

The products were analysed by gas chromatography: a Porapak-Q column at 353 K with an FID for C_1–C_4 hydrocarbons, and at 433 K for methanol, ethanal and ethanol; a Porapak-N column at 433 K with an FID for acetone and propanal; a TSG-1 on Shimarite-F column (from Shimadzu Co. Ltd.) at 393 K with a TCD for methanal; a molecular sieve 5A column at 323 K with a TCD for oxygen; and an active carbon column at 323 K with a TCD for H_2, CO and CO_2.

The atomic absorption analysis was carried out using an AA-8200 atomic absorption/flame emission spectrometer (Nippon Jarrell Ash Inc.). X-Ray fluorescence (XRF) analyses were carried out using KEVEX EDX-771 apparatus in the Environment Preservation Center of Kyoto University. The BET surface area of the catalyst was measured with a BELSORP 28, a microprocessor-controlled automatic system using N_2 at 77 K, from BEL Japan Inc. An X-ray diffraction study was performed using a Shimadzu XD-D1 with Cu-Kα emission in the range $5 < 2\theta$/degrees < 70. UV–VIS diffuse reflectance spectra were measured with a Perkin-Elmer Lambda-19 multipurpose spectrophotometer, in which reflected beams were gathered by an integrating sphere (100 mm id). A UV cell (10 mm × 40 mm, inner thickness 1.0 mm) equipped with a branched chamber and a stop valve was used in order to avoid any contact with moisture. The catalyst was heated in the branched chamber at 573 K under atmospheric pressure for 30 min, then evacuated at 823 K for 30 min, followed by the treatment under 150 Torr of oxygen at 823 K for 2 h. The catalyst was then transferred into the UV cell, and spectra were measured *in vacuo*. Magnesium oxide (Wako) was used as a reflectance standard. All the spectra were modified in terms of the Kubelka–Munk function. X-Ray photoelectron spectra (XPS) of the catalysts were acquired with an ULVAC-PHI 5500MT system equipped with a hemispherical energy analyser. The catalyst, pretreated in air at 823 K for 2 h, was mounted on indium foil and then transferred to an XPS analyser chamber. The residual gas pressure in the chamber during data acquisition was less than 1×10^{-8} Torr. The spectra were measured at *ca.* 173 K using Mg-K$\alpha_{1,2}$ radiation (15 kV, 400 W). The electron take-off angle was set at 45°. Binding energies were referenced to the Si 2p level of the catalyst support, SiO_2. The apparent shape and size of the catalyst particles were observed with a Hitachi S-2500 CX scanning electron microscope (SEM). The Raman spectra were obtained with an NEC GLG3260 Ar^+ ion laser (514.5 nm, 50 mW) and a Jobin-Yvon T-64000 spectrometer with CCD detector. The scattered light was collected in a back-scattering geometry. The accumulation time was 300 s. The sample was treated under 150 Torr of oxygen at 823 K for 2 h, evacuated at room temperature for 30 min, and then sealed in a tubular Raman cell made of Pyrex glass (8 mm od).

Results

Effect of method of catalyst preparation

The activities of various silica-supported group 5 and 6 metal oxide catalysts towards the photo-assisted oxidation of methane and ethane was examined at elevated reaction temperature, 493 K. Table 1 shows the yields of products from methane and ethane. The runs lasted 2 h for methane and 1 h for ethane. In the photooxidation of methane, silica-supported vanadium and molybdenum oxide catalysts showed significant activity. In particular, a silica-supported vanadium oxide catalyst (IW, 1.0 mol% V) was most effective, yielding 62 μmol of methanal together with 28 μmol of carbon oxides. The yield, based on methane feed, and the selectivity for methanal were 0.41 mol% and 69 mol%, respectively. For the photooxidation of ethane, both the silica-supported vanadium and molybdenum oxide catalysts showed high efficiency. Significant changes in the formation rate of the products were not observed during prolonged runs for 9 h, with both molybdenum and vanadium oxide catalysts. Note that, with molybdenum oxide catalysts, formation of methanal, the product *via* the dissociation of the carbon–carbon bond, was significant.

The effect of the loading level of vanadium species on the photooxidation of methane was examined using V_2O_5/SiO_2-IW catalysts at 493 K. As shown in Fig. 1(a), the rate of formation of methanal had a maximum value of 34 μmol h^{-1} (0.15 μmol h^{-1} m^{-2}, see also Table 2) at 0.6 mol% V, which corresponds to 76 mol% selectivity and 0.48 mol% one-pass yield. Turnover frequency (TOF) was 8.2 mol (mol V)$^{-1}$ h^{-1}. Further loading drastically decreased the rate of formation. The reaction of ethane also showed a similar dependence [Fig. 1(b)]. The reaction with the IW catalyst with 0.6 mol% V afforded the desired products in the highest yields for both reactants. The rate of formation of carbon oxides also showed similar behaviour.

Table 1 Photo-assisted catalytic oxidation of methane and ethane using silica-supported group 5 and 6 metal oxide catalysts at 493 K[a]

run	catalyst (prep., mol%[metal][b])	alkane (conversion %)	time/h	yield/µmol				selectivity for aldehydes (%)
				CH_3CHO	HCHO	CO	CO_2	
1	V_2O_5/SiO_2 (ED, 2)	CH_4 (0.48)	2	—	60	12	tr	83
2	V_2O_5/SiO_2 (IW, 1)	CH_4 (0.60)	2	—	62	16	12	69
3	V_2O_5/SiO_2 (SG, 1)	CH_4 (0.37)	2	—	46	4	6	82
4	Nb_2O_5/SiO_2 (IW, 2)	CH_4 (0)	2	—	tr.	0	tr	0
5	MoO_3/SiO_2 (ED, 1)	CH_4 (0.24)	2	—	26	6	4	72
6	V_2O_5/SiO_2 (ED, 2)	C_2H_6 (0.65)	1	41	9	0	7	93
7	V_2O_5/SiO_2 (SG, 1)	C_2H_6 (0.89)	1	62	7	1	2	98
8	MoO_3/SiO_2 (ED, 1)	C_2H_6 (0.77)	1	42	22	2	7	92
9	WO_3/SiO_3 (IW, 1)	C_2H_6 (0.04)	1	3	0	0	tr	≈100

[a] Amount of catalyst 0.025 g, W/F 0.71 g h mol^{-1}, alkane feed rate 7.5 mmol^{-1}, alkane : O_2 : He = 3 : 1 : 10. [b] Preparation method and loading level in preparation.

In order to investigate the effect of the pretreatment of the silica support, the reactions were performed using V_2O_5/SiO_2-IW (0.6 mol% V) catalysts prepared using silica calcined at various temperatures. As shown in Fig. 2, the amounts of methanal from methane decreased at higher calcination temperature, whereas those of ethanal from ethane increased. The V_2O_5/SiO_2 (calcined at 1023 K)-IW (0.6 mol% V) catalyst yielded 85 µmol of ethanal (0.43 µmol h^{-1} m^{-2}). Provided that the reaction requires one photon to produce one molecule of ethanal from ethane, this formation rate corresponds to *ca.* 7% of the number of photons (*ca.* 250–500 nm) irradiated into the catalyst layer as measured by chemical actinometry (*vide supra*). The yields of carbon oxides from methane also decreased with the use of calcined silica, thus the selectivity for methanal was nearly unchanged. On the other hand, the amounts of carbon monoxide and dioxide from ethane were almost constant, irrespective of the calcination temperature of the silica, implying improved selectivity for ethanal by high-temperature pretreatment.

Since the catalysts prepared by the sol–gel method were expected to have uniform surface vanadium species, their

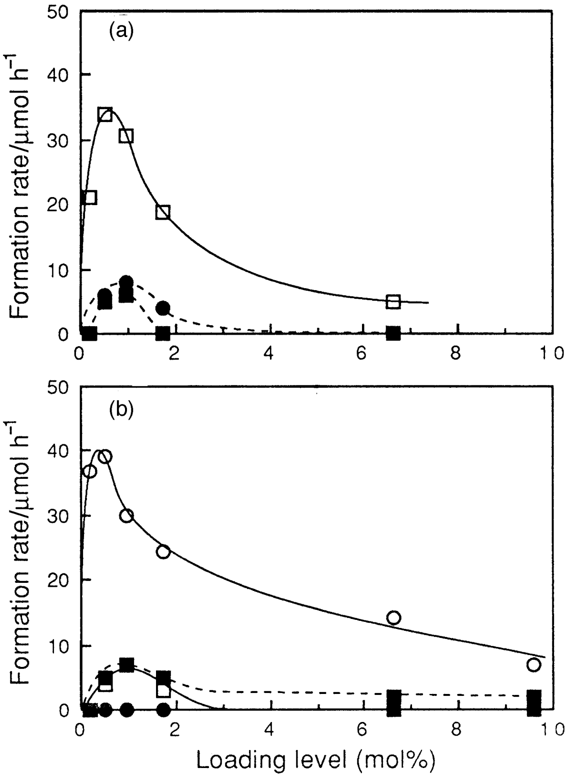


Fig. 1 Effect of loading level of V on photooxidation of (a) methane and (b) ethane using V_2O_5/SiO_2-IW catalysts: Rate of formation of (○) ethanal, (□) methanal, (●) carbon monoxide and (■) carbon dioxide. Amount of catalyst, 0.025 g; feed rate of alkane, 7.5 mmol h^{-1}; alkane : oxygen : helium = 3 : 1 : 10 in molar ratio; W/F, 0.71 g h mol^{-1}; 493 K.

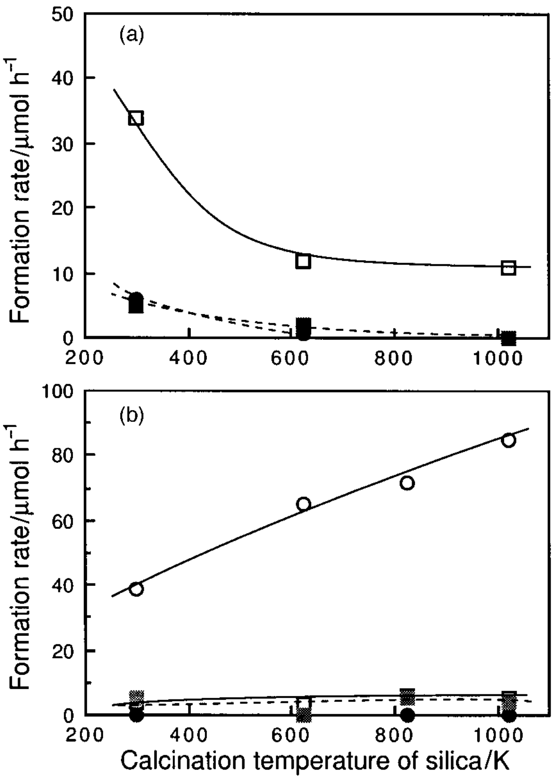


Fig. 2 Effect of calcination temperature of silica gel used for the preparation of the V_2O_5/SiO_2-IW (0.6 mol% V) catalysts on photooxidation of (a) methane and (b) ethane, Rate of formation of (○) ethanal, (□) methanal, (●) carbon monoxide and (■) carbon dioxide. Amount of catalyst, 0.025 g; feed rate of alkane, 7.5 mmol h^{-1}; alkane : oxygen : helium = 3 : 1 : 10 in molar ratio; W/F, 0.71 g h mol^{-1}; 493 K.

Table 2 BET surface areas of selected silica-supported vanadium oxide catalysts

catalyst (mol%)	BET surface area/m^2 g^{-1}
IW 6.6	230
IW 0.6[a]	200
IW 0.6	220
SG 4.0	480
SG 2.0	520
SG 1.0	580
SG 0.2	750

[a] Prepared using silica calcined in air at 1023 K for 2 h.

effects on the reaction of methane and ethane were examined. As shown in Table 1, runs 3 and 7, the SG catalyst generally showed high activities, especially towards the reaction of ethane. Fig. 3 shows the effect of increasing the concentrations of vanadium on the reactions of methane and ethane. For both reactions, the catalyst containing 1.0 mol% V showed the maximum yield of aldehydes. Further increasing the vanadium concentrations resulted in decreasing conversions, especially markedly in the case of methane. TOF of the catalyst containing 0.2 mol% V exhibited a much higher value, indicating that the catalysts with lower V concentration were suitable for both reactants. In every case examined, the selectivity for aldehyde formation was >90%. Most of by-products were carbon oxides. As can be seen in Fig. 3(c), the activities for the reactions with ethane per unit surface area of the SG catalysts were at best 0.11 μmol h^{-1} m^{-2}, and were generally lower than those of the IW catalysts [because of lack of BET surface area, the data for SG (4.9 mol%) catalysts were not included in Fig. 3(c)].

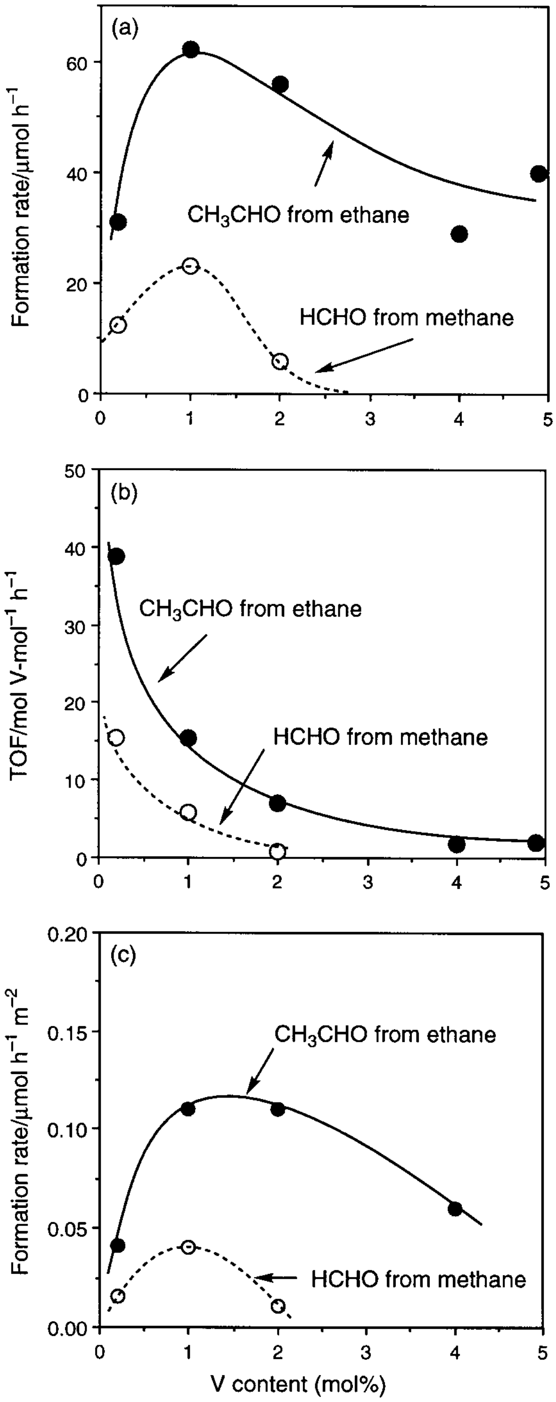


Fig. 3 Effect of content of vanadium species in the V_2O_5/SiO_2-SG catalysts on photooxidation of methane and ethane: (a) Rate of formation, (b) TOF and (c) rate of formation per unit surface area of (○) methanal from methane, (●) ethanal from ethane. Amount of catalyst, 0.025 g; feed rate of alkane, 7.5 mmol h^{-1}; alkane : oxygen : helium = 3 : 1 : 10 in molar ratio; *W*/*F*, 0.71 g h mol^{-1}; 493 K.

Effects of reaction conditions, addition of water and irradiation wavelength

As demonstrated previously,[20] the temperature crucially affected the reactions. In the photooxidation of methane using a silica-supported vanadium oxide catalyst (IW, 1.0 mol% V), the reaction at <400 K gave only trace amounts of the products. The yields of the products increased with increasing temperature. This is probably because of promotion of the desorption of water and the products from the surface. The yield of methanal showed a maximum at *ca.* 500 K, and decreased markedly at higher temperatures. The yields of carbon oxides also decreased above 500 K. In addition, formation of carbonaceous materials on the surface during reactions at high temperatures was not observed, since air oxidation of these used catalysts at 823 K for 1 h produced only a trace amount of carbon dioxide. These results indicate that the decrease in the yield of methanal above 500 K was not due to secondary deep oxidation of methanal. On the other hand, the ethane reactivity showed a less marked dependence on the reaction temperature. The reaction at *ca.* 350 K yielded 4 μmol h^{-1} of ethanal, and the rate gradually increased with increasing temperature, even at >500 K.

The effects of water vapour on the photooxidation of methane and ethane were examined using the V_2O_5/SiO_2 (IW, 0.6 mol% V) catalyst, as shown in Fig. 4. The amount of methanal from methane decreased drastically on introduction of water vapour. On the other hand, the amount of ethanal from ethane improved slightly in the presence of 9 Torr of water vapour. Further increase in the vapour pressure of water decreased the yields.

The photo-assisted oxidation of propane produced propanal, acetone, ethanal and carbon dioxide, the main products being propanal and ethanal. The rate of formation of carbon dioxide was 6 μmol h^{-1}, thus the selectivity for oxygen-containing chemicals was >90%. As shown in Fig. 5, the reaction of propane also showed a similar dependence on water

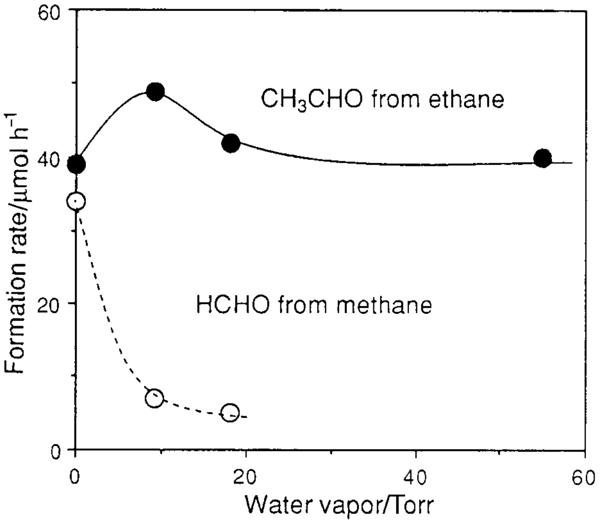


Fig. 4 Effect of water vapour on photooxidation of methane and ethane using the V_2O_5/SiO_2-IW (0.6 mol% V) catalyst: Rate of formation of (○) methanal from methane, (●) ethanal from ethane. Amount of the catalyst, 0.025 g; feed rate of alkane, 7.5 mmol h^{-1}; alkane : oxygen : helium = 3 : 1 : 10 in molar ratio; *W*/*F*, 0.71 g h mol^{-1}; 493 K.

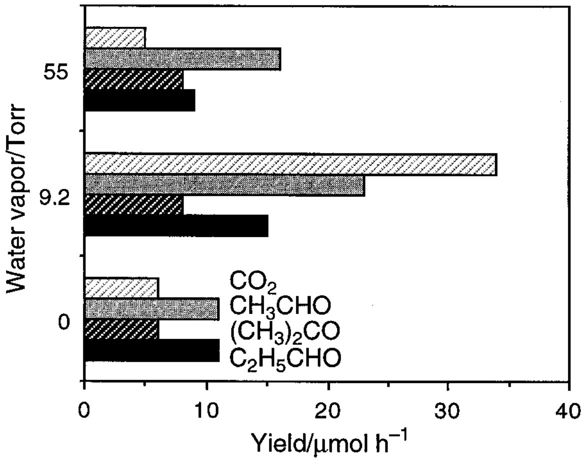


Fig. 5 Effect of water vapour on photooxidation of propane using the V_2O_5/SiO_2-IW (0.6 mol% V) catalyst. Amount of catalyst, 0.025 g; feed rate of propane, 7.5 mmol h^{-1}; propane : oxygen : helium = 3 : 1 : 10 in molar ratio; W/F, 0.71 g h mol^{-1}; 493 K; 1 h.

vapour to that of the reaction of ethane. The reaction was 9.2 torr of water vapour increased the rate of formation of the products, especially ethanal and carbon dioxide. Further addition of water vapour decreased the conversion of propane, but there were changes in the selectivities. The selectivity for ethanal increased further, whereas the formation of carbon dioxide decreased. These changes in the selectivities suggest variations in the active oxygen species or surface state of the catalysts (*vide infra*).

The effects of irradiation wavelength on photooxidation of methane and ethane using the V_2O_5/SiO_2-IW (0.6 mol% V) catalyst were investigated. The results are shown in Fig. 6. The amount of methanal formed by the photooxidation of methane decreased drastically by cutting off the light of wavelength shorter than 310 nm using a UV-31 filter. This indicates that, for the reaction of methane, irradiation with light of wavelength <300 nm was essential. On the other hand, the reaction of ethane when using a UV-31 filter produced a significant amount of ethanal. Even the reaction when using a UV-35 filter (passes $\lambda > 350$ nm) afforded a small amount of ethanal.

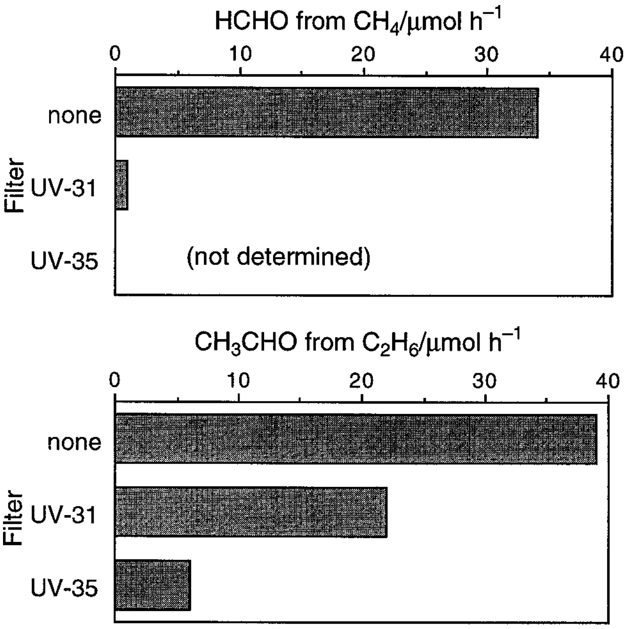


Fig. 6 Effect of irradiation wavelength on photooxidation of methane and ethane using the V_2O_5/SiO_2-IW (0.6 mol% V) catalyst. Amount of the catalyst, 0.025 g; feed rate of alkane, 7.5 mmol h^{-1}; alkane : oxygen : helium = 3 : 1 : 10 in molar ratio; W/F, 0.71 g h mol^{-1}; 493 K.

Analysis of the catalysts

Table 2 shows the BET surface areas of selected catalysts. For V_2O_5/SiO_2-IW catalysts of loading levels below 6.6 mol%, there were no significant changes in surface areas; they showed slightly lower surface areas than that of the parent silica support. The use of silica calcined at high temperature slightly decreased the surface area. These results indicate that surface area was not a significant factor. On the other hand, the SG catalyst with 0.2 mol% V showed a large surface area of 750 m^2 g^{-1}. However, increases in the concentration of vanadium oxide greatly decreased the surface areas. These marked changes in surface area would affect the surface concentration and dispersion of vanadium species and, eventually, the rate and selectivity of the reaction (*vide infra*).

The catalysts were analysed by means of Raman spectroscopy. Selected spectra of the IW catalysts are shown in Fig. 7. The V_2O_5/SiO_2-IW (0.6–1.7 mol% V) catalyst showed a Raman band at 1043 cm^{-1}, corresponding to isolated vanadium oxide (VO_4) surface species,[21,22] whereas, with the V_2O_5/SiO_2-IW (6.6 mol% V) catalysts the formation of V_2O_5 microcrystals (996 cm^{-1}, terminal V=O bond; 703 cm^{-1}, V—O—V vibrations) was observed, in addition to VO_4-type

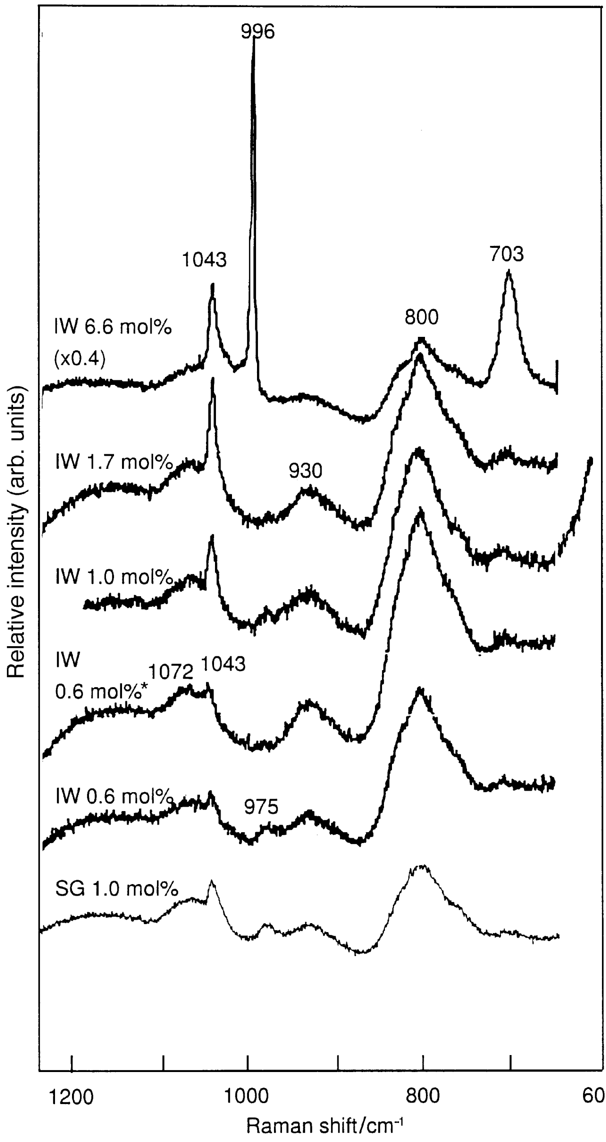


Fig. 7 Raman spectra under dehydrated conditions of the V_2O_5/SiO_2-IW and -SG catalysts. (*) prepared using silica calcined at 1023 K.

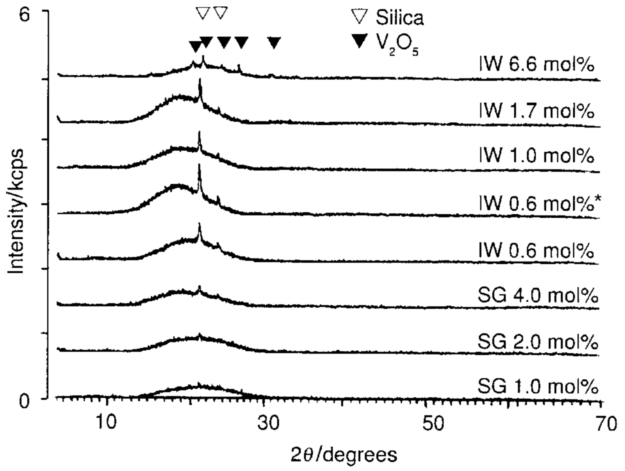


Fig. 8 XRD patterns of the V_2O_5/SiO_2-IW and -SG catalysts. (*) prepared using silica calcined at 1023 K.

species. Raman bands around 975 and 800 cm^{-1} were assigned to silanol groups and siloxane bridges, respectively.[22] Two weak Raman bands at around 1075 and *ca.* 930–910 cm^{-1} were observed, characteristic of SiO^- and $Si(O^-)_2$ functionalities.[22] Hence, peaks other than at 1043, 996 and 703 cm^{-1} can be assigned to the silica support. The spectra of V_2O_5/SiO_2-SG (1.0 mol% V) catalyst also showed a Raman band at 1043 cm^{-1} and none of bands corresponding to V_2O_5, indicating the formation of only four-coordinated vanadium oxide species.

Fig. 8 shows XRD patterns of the IW and SG catalysts. The formation of crystalline V_2O_5 was observed with the catalyst with 6.6 mol% V. On the other hand, the spectra of the catalysts of lower loading level did not show any diffraction patterns other than the common patterns of crystalline silica. The SG catalysts examined also did not show any patterns except for those of crystalline silica, indicating the absence of microcrystals of V_2O_5.

XPS analysis of the catalysts revealed the presence of Si, O, C and V on their surface. There were no signs of other elements by wide-range survey analysis. Fig. 9(a) shows the atomic ratio of each of the elements on the surface, determined by peak intensities of Si 2p, O 1s, C 1s and V 2p *vs.* overall atomic ratio (N_V/N_{Si}). These atomic ratios were calculated based on sensitivity factors reported for the spectrometer used in this study.[23] For all the catalysts examined, most of their surface was composed of SiO_2, together with small amount of carbon and vanadium. As shown in Fig. 9(b), which shows the relative molar ratio of V and Si *vs.* the overall atomic ratio (N_V/N_{Si}), the IW catalysts of 0.2 mol% V showed the highest vanadium observability. Combined with the results of XRD and Raman analyses, the formation of rather accumulated vanadium species on the surface with IW catalysts of high loading level is demonstrated, whereas the IW catalysts of low loading level and the ED catalyst seem to have more dispersed species on their surface. Note that there were no significant differences in the surface atomic ratio of V to Si between IW catalysts of 0.6 mol% V prepared using silica with or without calcination. They showed the same atomic ratio of vanadium to silicon (0.84 atom%). Fig. 9(c) and (d) show the atomic ratios of each of the elements and the relative ratio of the molar ratio of V and Si for SG catalysts, respectively. There were similar tendencies in the vanadium observability to those of the IW catalysts, indicating the formation of rather accumulated vanadium species with SG catalysts of high vanadium concentration.

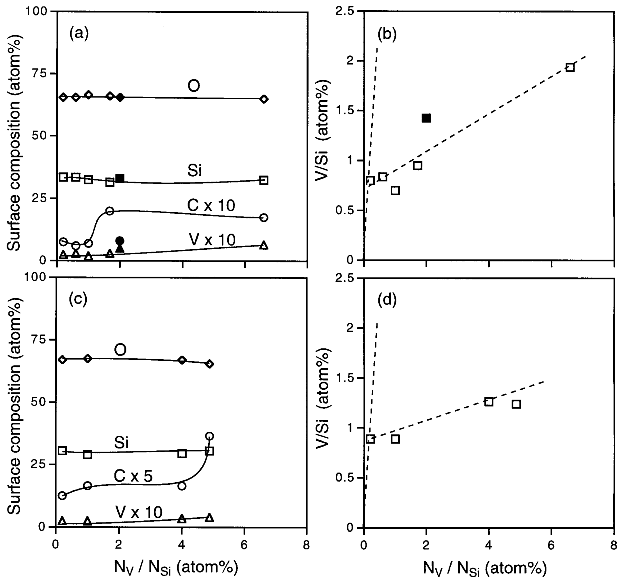


Fig. 9 (a) Surface composition and (b) V/Si atomic ratio of IW (open symbols) and ED (filled symbols) catalysts, (c) surface composition and (d) V/Si atomic ratio of SG catalysts, measured by XPS.

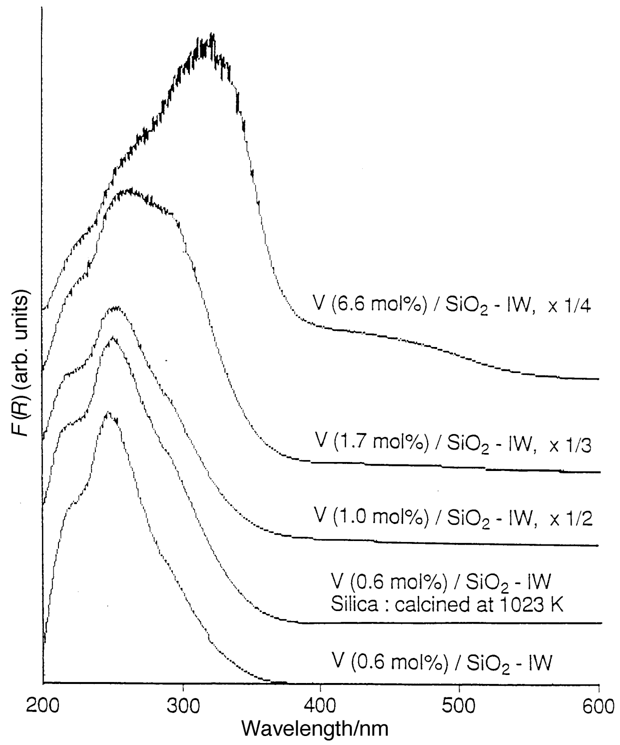
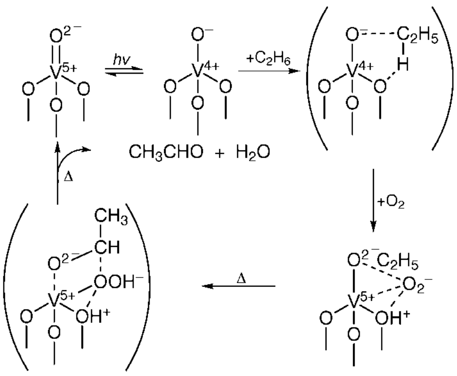


Fig. 10 UV diffuse reflectance spectra of V_2O_5/SiO_2-IW catalysts under dehydrated conditions

Fig. 10 shows selected UV diffuse reflectance spectra of the catalysts. A major absorption band around 260 nm was detected for all the catalysts. With V_2O_5/SiO_2-IW (1.7 mol% V) and -IW (1.0 mol% V) catalysts a shoulder peak at *ca.* 300 nm was also observed. On the other hand, the catalyst with 6.6 mol% V exhibited a strong absorption band at *ca.* 330 nm, in addition to that at 260 nm. Note that there was weak absorption at 300 nm in the spectrum of the 0.6 mol% V catalyst using calcined silica, whereas the spectrum of the catalyst using silica without calcination showed no such shoulder.

Discussion

One of the probable reaction mechanisms, based on that proposed by Kazansky and coworkers[5] on the basis of Hartree–Fock calculations is shown in Scheme 1. As a first step, the surface four-coordinated vanadium oxide having a V=O double bond is excited by irradiation to form a charge-transfer complex. An oxygen is trapped by a positive hole to produce a strongly electrophilic O^- radical species, and an



Scheme 1

electron transfers to the vanadium. Such excitation has been generally accepted for the photooxidation of various alkenes.[24] Some of activated species return to the ground state by recombination of the hole and the electron. An alkane is adsorbed on the photoactivated species and its C—H bond is activated. Molecular oxygen would adsorb onto an electron-rich site of the intermediate. Abstraction of another hydrogen by an adsorbed oxygen species would produce aldehydes, together with reoxidation of the surface species. At relatively high reaction temperature, transformation of the intermediate to aldehyde, desorption of the products and water, and reoxidation of the vanadium surface species would be promoted.

According to the catalytic runs and XRD study, formation of crystalline V_2O_5 seems not to have a positive effect in the present reactions. Studies of the Raman spectra indicate that in general four-coordinated vanadium oxide species seem to be necessary. In addition, XPS and catalytic runs suggest that formation of more dispersed species on the surface definitely affects the yields of aldehydes.

The results in Fig. 3 indicate that SG catalysts with a lower concentration of vanadium species yield aldehydes in higher yields, although the activities per unit surface area were generally lower than those of the IW catalysts. Since SG catalysts with lower V concentration showed higher surface areas, the density of the surface vanadium species would be decreased with decreasing concentration. In addition, the XPS study suggests the formation of rather accumulated vanadium species on the surface of the catalysts with high vanadium concentration [Fig. 9(d)]. These results suggest the effectiveness of vanadium species in low density for aldehyde formation.

However, the reactions with methane and higher alkanes are sometimes differently affected by the reaction conditions and catalyst preparation. In general, the reaction of methane was apt to be very sensitive, and very delicate tuning of the surface species seems to be required. For example, although calcination of the silica support showed completely different effects between the reactions of methane and those of ethane, no significant differences were found in the spectroscopic study. The BET surface area of the catalyst using non-calcined silica and that using calcined silica were 220 and 200 m^2 g^{-1}, respectively. These catalysts showed similar surface atomic ratios of V to Si as measured by XPS. There were no significant differences in the Raman spectra. The only difference was in the UV–VIS diffuse reflectance spectra. As shown in Fig. 10, a shoulder absorption at 300 nm was characteristic for the catalyst using calcined silica. Previous studies of UV spectra[25] suggest that a shoulder absorption at 300 nm is responsible for rather aggregated non-octahedral vanadium species. Formation of such aggregated species is reasonable, since calcination at high temperature would reduce the number of surface hydroxy groups.

Combined with the dependence on the irradiation wavelength, we can conclude that there are differences in the most suitable surface state of the catalysts and/or the conditions between the reaction of methane and other light alkanes. Only very highly isolated vanadium oxide surface species, which absorb light of wavelength <300 nm, would show catalytic activity towards the selective photooxidation of methane, whereas rather accumulated vanadium surface species, not crystalline V_2O_5, would activate other light alkanes.

On the other hand, the reaction of methane was inhibited by the addition of water, whereas the reaction of ethane was sometimes slightly promoted. In addition, in the photooxidation of propane, the rate of formation of the products increased greatly in the presence of a small amount of water, and changes in selectivities were observed. In particular, the yields of carbon dioxide and ethanal were markedly promoted. Further addition of water vapour, conversely, decreased the yields. These results suggest changes in the active oxygen species and/or surface state which governed the reactions.

These phenomena were most likely due to OH radicals on the surfaces. Enhancement of photoreactions by water vapour have been previously observed *e.g.* on titanium oxide.[26] Similar dependences of the oxidation rate on humidity have been reported and explained as being the result of competitive absorption of water and reactants.[26] On the other hand, the addition of water would cause surface hydration, which was reported to increase the coordination number of the vanadium species and weaken the V=O double bond.[27] Provided that, for the reaction with methane, the presence of four-coordinated species on the surface was crucial, and surface OH radicals did not show significant activity, then it would be reasonable for the addition of water to retard markedly the formation of methanol from methane.

Conclusions

Selective photooxidation of light alkanes, mainly methane and ethane, into the corresponding aldehydes was achieved using silica-supported vanadium oxide catalysts under UV irradiation at *ca.* 500 K. For the photooxidation of methane, the V_2O_5/SiO_2-IW (0.6 mol% V) catalyst showed the highest activity. For the reaction with ethane, the IW catalyst prepared using calcined silica showed promoted activity. The catalysts prepared by the sol–gel method also showed activity, especially for the reaction of ethane, although the activity per unit surface area was generally lower than for the IW catalysts. While the reaction of methane was inhibited by the addition of water vapour, the photooxidation of ethane and propane was promoted in the presence of a controlled amount of water vapour. The reaction with methane required UV irradiation of wavelength <310 nm, whereas the reaction with ethane or propane proceeded on irradiation at longer wavelength. According to the surface analysis of the catalysts, only isolated four-coordinated vanadium oxide surface species were considered to show catalytic activity towards the photooxidation of methane, while rather accumulated vanadium surface species were shown to be active for the photooxidation of other light alkanes.

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