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V_2O_5/SiO_2 Catalysts Modified by Na^+ Ions: Surface Characterization by Spectroscopic Methods and Photoassisted Oxidation of 2-Propanol and Propene

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Silica-supported vanadium oxide prepared by impregnation of silica with a mixed solution of NaOH and NH_4VO_3 exhibits a high activity in the photooxidation of 2-propanol and propene as well as improves selectivities to propanone from 2-propanol and to acraldehyde from propene. The amount of sodium ions added affected the selectivity in the photooxidation of propene significantly but did not affect that of 2-propanol. In both reactions, the highest activity was observed for the catalyst containing 1 wt% Na_2O. UV–Vis spectra of the catalysts show that there are three different phases of vanadates on the silica surface, namely a polymeric phase and two tetrahedral phases. One of the tetrahedral phases exhibits an absorption band at 315 nm, which is an active species in the photocatalysis. By comparison of the results of the reactions, it is concluded that the addition of sodium ions alters the composition of surface phases. Addition of an appropriate amount of sodium ions maximizes the fraction of the active phase on the surface and enhances photocatalytic activity.

INTRODUCTION

UV-irradiated vanadium oxide supported on silica catalyzes oxidations of carbon monoxide (*1, 2*), alkenes (*3, 4*), and alkanes (*5*) at room temperature. These photocatalytic reactions are also catalyzed by other *n*-type semiconductor metal oxides such as TiO_2 (*6*). However, V_2O_5/SiO_2 has the characteristic of producing aldehydes selectively in the photooxidation of propene at a high level of conversion. This is in marked contrast to the catalysis by TiO_2 which leads to almost total oxidation even at a low conversion level (0.055%) (*7*). On the other hand, bulk V_2O_5 exhibits a quite poor photoactivity (*7*). Therefore, dispersion of vanadium oxide on a silica support is important for preparing a catalyst active for the selective photooxidation.

Dispersion of an active metal oxide on a carrier not only increases the surface area of active metal oxide but can also result in formation of surface species with particular structures. Vanadium oxide supported on silica has been proposed to have structures different from those of the bulk oxide and many studies on it have been reported (*8*). The local structure must affect the activity of vanadium oxide. Furthermore, it is known that a composite compound of two kinds of metal oxides very often exhibits stronger surface acidity than that of single oxide and the acidic property sometimes influences the reactivity of the solid, especially the selectivity (*9*). Thus, an interaction between vanadium oxide and silica in V_2O_5/SiO_2 may generate acid sites and such a surface acid property could be a controlling factor in photooxidation, but little work has been done on the relation between acidity and photocatalysis (*10*).

There have been many papers on photo-

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oxidation of alcohols catalyzed by solid catalysts (*11, 12*) and some of them have reported that dehydration, which usually proceeds on an acid site, is present as a side reaction. Nevertheless, not much attention was paid to this result.

We carried out photooxidation of 2-propanol over V_2O_5/SiO_2 and found that oxidative dehydrogenation is much enhanced by UV irradiation of the catalyst under an oxygen atmosphere at room temperature. This dehydrogenation accompanied dehydration to produce propene as observed in the case of photooxidation of 2-propanol over TiO_2 (*11*). We presumed that dehydration proceeded on acid sites and therefore carried out the reactions over pyridine-poisoned or ammonia-poisoned V_2O_5/SiO_2 in order to suppress its acidity. Such poisoning inhibited the dehydration as expected, but the yield of propanone decreased simultaneously (*13*). Then, we tried another type of catalyst: sodium-ion-added V_2O_5/SiO_2. The catalyst exhibited a high activity as well as high selectivity to propanone. In addition, it was found that addition of sodium ions brought about improvement in selectivity in photooxidation of propene.

In the present paper, we describe the effect of addition of sodium ions on the photooxidation of 2-propanol and propene mentioned above, and discuss the nature of the active species.

EXPERIMENTAL

Materials. Reactants (propene, 2-propanol, and oxygen), pyridine, silicon tetraethoxide, and ammonium metavanadate were commercially supplied. V_2O_5 was prepared by the thermal decomposition of ammonium metavanadate in a dry air stream at 673 K (*14*). Gaseous reactants were purified by vacuum distillation several times at low temperatures. Pyridine and 2-propanol were dehydrated and distilled. The alkoxide was distilled *in vacuo* twice. Silica was prepared by the hydrolysis of the alkoxide as described elsewhere (*15*). Reference compounds ($NaVO_3 \cdot 12H_2O$ and $Na_3VO_4 \cdot xH_2O$, $x = 3$–5) for UV and vis spectra were of an extrapure grade and were used without purification. ^{18}O-labeled propanone was synthesized as described previously (*16*).

Catalysts. The catalysts were prepared by impregnating the silica mentioned above with aqueous solutions containing the desired amounts of vanadium and sodium, followed by calcination in a dry air stream at 773 K for 5 h. The solutions for impregnation were prepared by dissolving ammonium metavanadate in proper amounts of 0.1 mol dm^{-3} NaOH solution. V_2O_5 content was 5% by weight for each catalyst. Contents of sodium ions were 0 wt% (VS), 0.1 wt% (VSS01), 1 wt% (VSS1), 1.9 wt% (VSS2), and 5 wt% (VSS5) as Na_2O.

Pretreatment of the catalysts. The catalyst surface was conditioned by treatment with 60 Torr (1 Torr = 133.3 Pa) of oxygen gas at 673 K for 2 h, followed by evacuation at the same temperature for 30 min prior to each run and measurement.

Reactions. The reactions were performed in a conventional closed circulating system described elsewhere (*1*). UV light was provided at room temperature from a 250-W Hg lamp through a glass filter transparent to wavelength $\lambda > 300$ nm. UV irradiation times were 30 min for propene photooxidation and 60 min for 2-propanol photooxidation. After each run, the catalyst bed was heated to 473 K for collecting polar products such as aldehydes and ketones which are tightly adsorbed on the catalyst at room temperature. The desorbed products were frozen out in a trap cooled by liquid nitrogen (*3*), and analyzed by GLC.

Pyridine desorption. Pyridine was adsorbed on a catalyst placed in a glass vessel fitted with a stopcock. The vessel was cooled by liquid nitrogen, evacuated for several minutes, closed and left under ambient conditions. Then the temperature of the catalyst bed was raised stepwise by 50 K *in vacuo*, the desorbed pyridine being

TABLE 1

Photooxidation of 2-propanol[a]

Catalyst[b]	Yields (μmol)[c]				
	$CH_2{=}CHCH_3$	CH_3COCH_3	CH_3CHO	$2C_3H_7OH$	C_3/C_3OH[d]
VS	19.5(38.1)	12.5(1.1)	0.34	3.8(8.0)	5.1(4.8)
VSS01	16.3(33.8)	15.8(1)	0.37	7.1(17.5)	2.3(1.9)
VSS1	7.7(16.9)	20.4(2.0)	0.42	13.1(30.8)	0.6(0.6)
VSS2	3.7(5.4)	16.7(2.0)	0.34	21.9(38.4)	0.2(0.1)
VSS5	0.1(0.0)	3.3(0.6)	0.00	34.6(44.8)	—
VS[e]	35.4	1.1	0.00	10.5	0.5
SiO^2	0.2	0.0	0.00	48.8	—

[a] Catalyst, 500 mg; irradiation time, 60 min; $2C_3H_7$, 50.0 μmol; O_2, 150 μmol.

[b] See text.

[c] Values in parentheses are those obtained in the dark reactions. CH_3CHO could not be detected in the dark reactions.

[d] The ratio of yields of $CH_2{=}CHCH_3$ to $2C_3H_7OH$.

[e] This run was carried out with a glass filter transparent at $\lambda > 390$ nm.

collected by the liquid nitrogen trap, and the amount was measured volumetrically.

Infrared spectroscopy. Spectra were recorded in a transmission mode using a Nicolet DX-20B Fourier transform IR spectrometer. A catalyst sample (20 mg) was pressed into a disk (20 mm diameter) and placed in an *in situ* cell with CaF_2 windows.

UV and visible spectroscopy. Spectra were recorded with a Shimadzu MPS-2000 spectrometer equipped with a diffuse reflectance attachment. The baseline variation by the catalyst support was corrected by the spectra of silica for the catalyst samples and MgO for the reference samples. The catalyst powders were placed in a quartz cell and conditioned as mentioned above before measurements were taken. The absorption curve was obtained by calculating the logarithm of reflectance: $A = \log(1/R_\infty)$. Here reflectance R_∞ is considerably smaller than 1.0 so that $1/R_\infty$ can be regarded approximately as a Kubelka–Munk function (*17*).

Estimation of the number of active surface V=O species. The isotopic oxygen heteroexchange between propanone and lattice oxygen of the catalyst was utilized for the determination of the number of active V=O species of the catalyst. The procedure was reported previously (*6*).

RESULTS

Photooxidation of 2-Propanol

The reaction products were propanone, ethanal, propene, and carbon dioxide. Silica was almost photoinactive. Product yields and the amounts of unreacted 2-propanol are shown in Table 1. By comparison of the results under UV irradiation and those in the dark and/or under light irradiation ($\lambda > 390$ nm), it is obvious that UV irradiation enhanced the production of propanone and ethanal significantly. The addition of sodium ions affected yields of these compounds, especially in the case of photooxidation. As shown in Fig. 1a, the yields changed in a similar manner for both the products; they increased with the amount of sodium ions added up to 1 wt% Na_2O and then decreased. The other main product was propene, the yield of which was reduced by UV irradiation. It should be noted that the ratio of [produced propene]/[unreacted 2-propanol] is almost unaffected by UV irradiation (last column of Table 1). (A slightly larger value under irradiation than

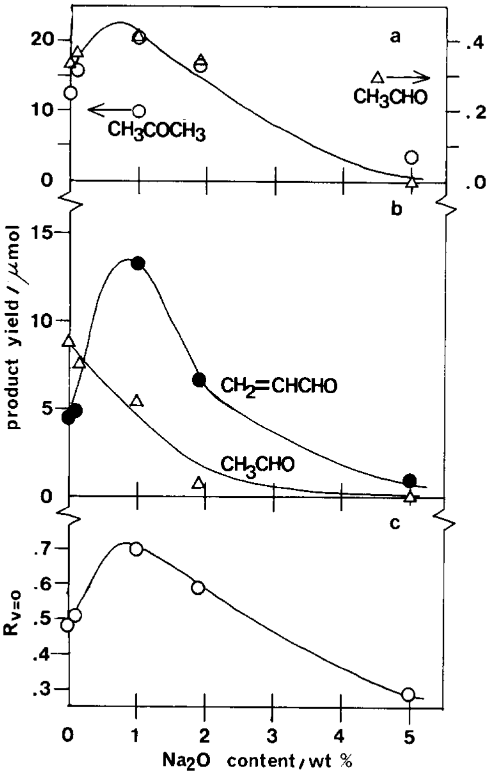


FIG. 1. Product distribution of photooxidations and $R_{V=O}$ plotted against Na_2O content of the catalysts. (a) The result of photooxidation of 2-propanol taken from Table 1; (b) the result of photooxidation of propene taken from Table 2; (c) $R_{V=O}$.

in the dark is presumed to result from a rise in temperature of the catalyst by irradiation.) Furthermore, the ratio decreased with the amount of Na_2O added. The results suggest that propene is not formed by the competitive reaction in the photooxidation but by thermal dehydration of unreacted 2-propanol adsorbed on acid sites; the dehydration proceeds mainly in the product-collecting process. This conclusion is consistent with that proposed by Djeghri and Teichner (*10*) for dehydration of alcohol during photooxidation over TiO_2, although no report dealing with the same system as ours has been published to our knowledge.

Photooxidation of Propene

The main products are ethanal and acraldehyde, with a small amount of propanal as already reported (*3*). Silica was photoinactive. Formation of carbon dioxide by total oxidation was scarcely observed (less than 10%). The results are shown in Table 2 and the yields of acraldehyde and ethanal are plotted against Na_2O content in Fig. 1b. It is noteworthy that the yield of ethanal decreased monotonically with the Na_2O content of the catalyst, whereas the dependence of the yield of acraldehyde is similar to that of ethanal and propanone in 2-propanol photooxidation (Fig. 1a).

Acidity of the Catalyst

The surface acidic property was examined by IR absorption spectroscopy and thermal desorption of adsorbed pyridine.

Figure 2 shows the IR absorption spectra of VS, VSS01, VSS1, and SiO_2 in contact with pyridine. The spectrum of pyridine observed on silica is rather simple, reflecting the fact that only weak acid sites exist on the silica surface (weak interaction with pyridine). The observable bands at 1446, 1489, and 1596 cm^{-1} are due to hydrogen-bonded pyridine (HPy) (*9*). By contrast, the spectrum on VS is complicated: bands at 1446, 1489, 1578, and 1608 cm^{-1} due to coordinatively bonded pyridine (LPy) show the existence of Lewis acid sites and the broadness of the band at 1446 cm^{-1} results

TABLE 2

Photooxidation of Propene[a]

Catalyst[b]	Conversion[c] (%)	Selectivity (%)[d]	
		$CH_2=CHCHO$	CH_3CHO
VS	16.3	27.6	54.6
VSS01	14.0	35.0	55.0
VSS1	21.2	62.7	25.9
VSS2	8.0	83.8	10.0
VSS5	1.3	76.9	7.7
SiO_2	0.0	—	—

[a] Catalyst, 500 mg; irradiation time, 30 min; $CH_2=CHCH_3$, 100 μmol; O_2, 100 μmol.

[b] See text.

[c] Based on $CH_2=CHCH_3$.

[d] Other minor products were C_2H_5CHO, CH_3COCH_3, and CO_2.

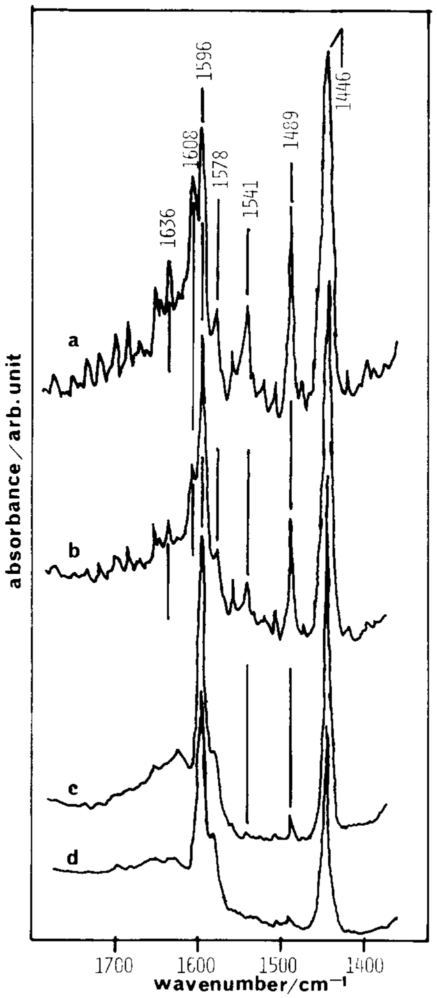


FIG. 2. IR spectra of the catalysts after adsorbing pyridine. (a) VS, (b) VSS01, (c) VSS1, (d) SiO_2.

from overlapping of bands due to LPy and HPy. Bands at 1489, 1541, and 1636 cm^{-1} are due to pyridinium ion (BPy), proving the existence of Brønsted acid sites. The relative intensities of these bands due to chemisorbed pyridines (LPy and BPy) are reduced by addition of Na_2O as indicated in the case of VSS01. The spectral feature on VSS1 is essentially the same as that on SiO_2. Evidently, addition of 1 wt% Na_2O is enough to reduce the acidity of 5 wt% V_2O_5/SiO_2 catalyst to the same level of silica. The thermal desorption profiles of pyridine shown in Fig. 3 also support the above conclusion. In the cases of VSS1 and silica, more than 80% of the adsorbed pyridine was desorbed by evacuation at temperatures below 373 K, while in the cases of VSS01 and VS, the peaks in desorption profiles shifted to higher temperatures and exhibited tailing. The amounts desorbed at temperatures above 373 K for VS are larger than those for VSS01, indicating that sodium addition reduces both the strength and the amount of acid sites.

UV and Visible Spectra (UVS) of the Catalysts

Electronic spectroscopy can be applied to the characterization of supported vanadium oxides (*18–20*). We also used UVS in this work, and the spectra of the catalysts are shown in Fig. 4. We can recognize three bands: A_v in the visible region (400–500 nm), A_{315} centered at 315 nm and A_{260} at 260 nm. The spectrum of V_2O_5 illustrated in Fig. 5 exhibits band A_v, the edge of which at ca. 530 nm corresponds to the energy gap between the valence band of O 2*p* and the conduction band of V 3*d* (*21*). Band A_v is indicative of the presence of polymeric vanadate with an energy band structure

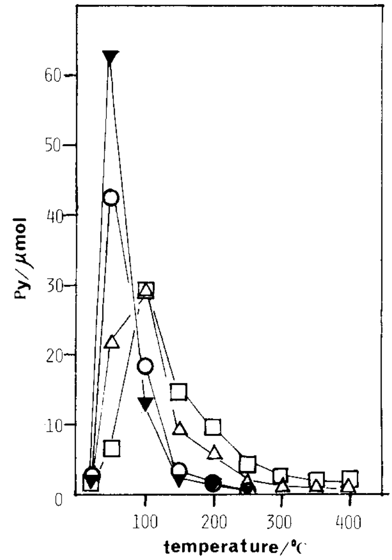


FIG. 3. Thermal desorption profile of pyridine. ○, SiO_2; □, VS; △, VSS01; ▼, VSS1.

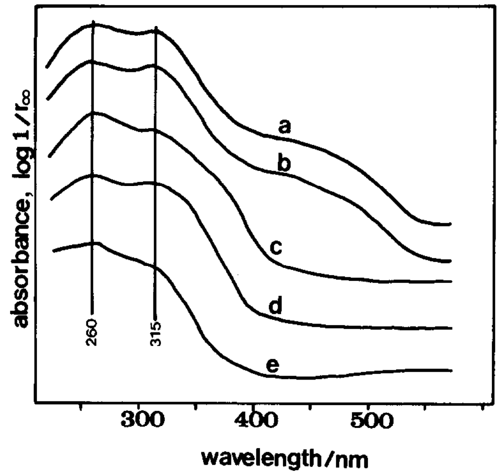


FIG. 4. UV–vis spectra of (a) VS, (b) VSS01, (c) VSS1, (d) VSS2, (e) VSS5.

similar to that of V_2O_5. This assignment is in agreement with that by Hanke *et al.* (*18, 19*). Band A_v can also be seen in the spectrum of VS. On the other hand, in the series of VSS catalysts, the band intensity in the visible region is reduced and the band finally vanishes leaving bands A_{315} and A_{260} with an increase in the amount of sodium ions. These two bands can be observed clearly in the spectra of VSS1 and VSS2. The disappearance of band A_v in the case of VSS01 may be related to the acid property of VSS1 mentioned above. In the spectrum of VSS5, band A_{315} is found only as a shoulder on band A_{260}. The change of intensity of band A_{315} by addition of sodium ions is closely related to the change of photocatalytic activity of the catalysts. Thus, the presence of species responsible for band A_{315} is important in photooxidation over V_2O_5/SiO_2.

The atomic ratios of Na to V in VSS2 and VSS5 are very close to those of $NaVO_3$ and Na_3VO_4 and it is possible that these compounds are formed on the silica surface. In Fig. 5, the spectra of these sodium vanadates are also shown. The spectrum of Na_3VO_4 has maximum absorption at 290 nm as already reported by Hanke *et al.* (*18*) and is very different from those of VSS catalysts. The spectrum of $NaVO_3$ has two maxima at 275 and 340 nm. This looks similar to the spectra of VSS1, VSS2, and VSS5, but the peak positions are different, indicating that the formation of $NaVO_3$, if any, is negligible.

Number of Active Surface V=O Species

The number of active surface V=O species of each catalyst was estimated by an oxygen exchange reaction and Fig. 1c shows $R_{V=O}$ (the ratio of the number of the exchangeable exposed V=O species to the number of vanadium ions). The small value of $R_{V=O}$ at low loading of Na_2O results from the presence of bulk vanadium oxide suggested by a clear absorption band A_v in UVS. With the content of Na_2O to 1 wt%, $R_{V=O}$ increases, corresponding to a gradual decrease in the absorption intensity of band A_v. Then $R_{V=O}$ decreased at high contents of Na_2O. The yields of oxygenates in the photocatalytic reactions are closely related to the change in the $R_{V=O}$ value as shown in Fig. 1. The decrease in $R_{V=O}$ at high contents of Na_2O is due either to the generation of vanadates inactive for the exchange reaction or to a decrease in the number of surface vanadates.

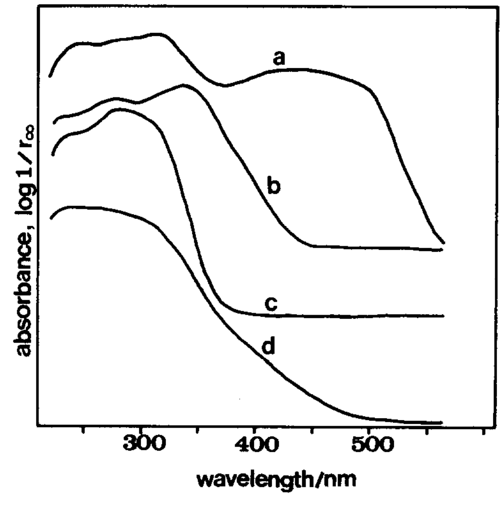
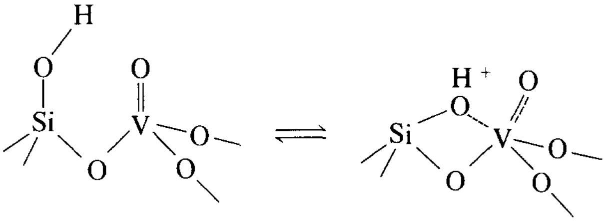


FIG. 5. UV–vis spectra of (a) V_2O_5, (b) $NaVO_3$, (c) Na_3VO_4, (d) V_2O_5/Al_2O_3.



SCHEME 1

DISCUSSION

Acid Site

IR spectra of adsorbed pyridine indicate the presence of both Lewis and Brønsted acid sites on silica-supported vanadium oxide catalysts. The Lewis acid center is naturally assignable to a vanadium ion on the surface. A Brønsted acid site is easily generated by the adsorption of a water molecule on a Lewis acid site. In the present case, however, the catalyst was evacuated at 673 K prior to pyridine adsorption and weakly adsorbed water molecules were desorbed at similar high temperatures. In previous work (*22*) on a quantum-chemical approach to the solid acidic property, it has been proposed that a Brønsted acid site is generated by the interaction between a Lewis acid site (a metal cation) and its adjacent OH group as shown in Scheme 1, and the strength of the Brønsted acid site is dominated by the strength of the Lewis acid site. A decrease in the number of Brønsted acid sites with the addition of sodium ions can be explained by the substitution of a proton by a sodium ion. Such inverse cation exchange is carried out to generate solid acid sites in zeolites (e.g., NaY → HY). However, such cation exchange does not result in a decrease in either Lewis acid strength or the number of its acid sites.

Prior to discussing the change in Lewis acidity, we should consider how a sodium ion was incorporated in the catalyst. As described above, acidity of the catalyst reaches the same level as that of silica at 1 wt% Na_2O corresponding to the atomic ratio Na/V = 1. Judging from the results of the reactions and the change in UVS, surface segregation of sodium ions does not occur and it is probable that sodium ions are adjacent to vanadium ions. Both cations are supposed to be interacting with each other through oxygen anions. We propose two possible routes where sodium ions are incorporated as shown in Scheme 2. The first route may occur during an impregnation step and the second during a calcination step.

Such adjacent sodium ions possibly have an effect on vanadium ions to change the Lewis acidity. In order to examine the electronic effect, we carried out molecular orbital calculations. Figure 6 shows the cluster models and charge on each atom. Models (O), (I), and (II) correspond to surface vanadium oxide unaffected by sodium ions, species *1* and *2* in Scheme 2, respec-

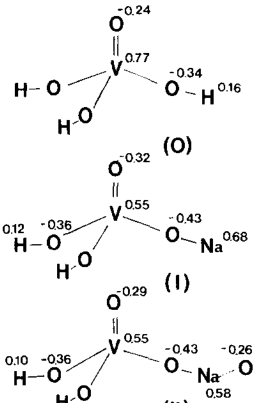
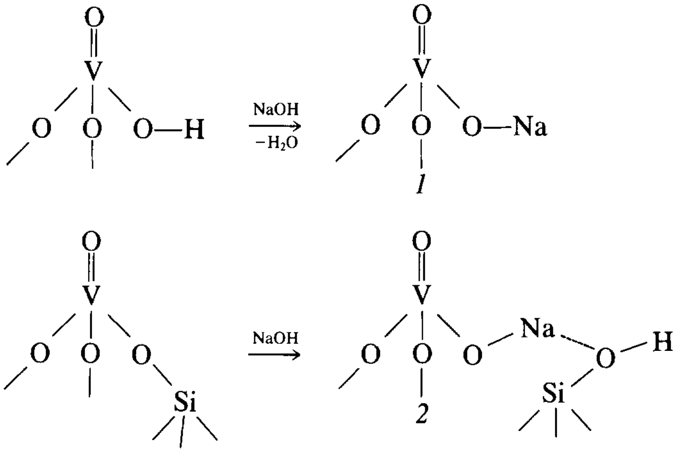


FIG. 6. Models used in the calculation. Model (0) is the VO_4H_3 free cluster. Bond lengths are $r(V{=}O)$ = 1.54 Å, $r(V{-}O)$ = 1.80 Å, $r(O{-}H)$ = 1.10 Å, $r(O{-}Na)$ = 1.90 Å.



SCHEME 2

tively. In our recent ab initio calculation (*23*) dealing with the interaction between a vanadium oxide cluster and supports like silica and alumina, it was found that the VO_4H_3 cluster, model (O), can be representative of a tetrahedrally coordinated vanadium ion supported on silica. As indicated in Fig. 6, it is evident that the positive charge on a vanadium atom decreases under the influence of a sodium atom in both cases of models (I) and (II). Negative charge is transferred from a sodium atom to a vanadium atom through the bridged oxygen species, and negative charge on the bridged oxygen increases to generate basic sites. Generally, charges on the atoms are closely related to acidity and basicity. However, the charge on an atom is not always a good index of the acid/base strength; the energy level of the LUMO (lowest unoccupied molecular orbital) or the HOMO (highest occupied MO) is a better index (*22*). Figure 7 shows the energy levels of the HOMO and LUMO for the three models. The HOMO and LUMO of model (O) consist of nonbonding orbitals on bridged oxygens and mainly vanadium 3*d* atomic orbitals, respectively, showing that bridged oxygen atoms and vanadium atoms are base and acid sites, respectively. The LUMOs of models (I) and (II) lie at higher levels by ca. 2 eV than that of model (O) and the LUMOs consist of mainly the sodium 3*s* atomic orbital. The unoccupied MOs localized on a vanadium atom of model (I) and (II) are found at higher energy levels than the HOMOs. The result indicates that acid strength of a vanadium ion decreases by the influence of an adjacent sodium ion. On the other hand, the HOMOs of models (I) and (II) lie at higher levels by ca. 4 eV than that of model (O) and the HOMOs are localized on an oxygen atom bonded to a sodium atom, showing that the bridged oxygen atom can work as a basic site.

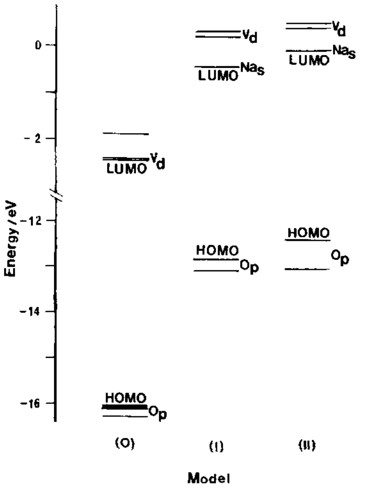
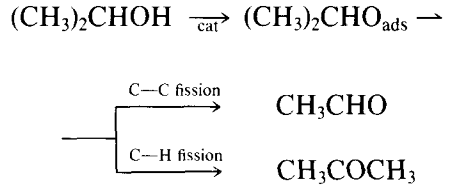


FIG. 7. The energy levels of HOMOs and LUMOs of the clusters.



$$(CH_3)_2CHOH \xrightarrow[cat]{} (CH_3)_2CHO_{ads} \rightarrow \begin{cases} \xrightarrow{C\text{—}C \text{ fission}} CH_3CHO \\ \xrightarrow{C\text{—}H \text{ fission}} CH_3COCH_3 \end{cases}$$

SCHEME 3

The results obtained by CNDO/2 calculation suggest that vanadium ions became less acidic by the electron transfer from adjacent sodium ions through V–O–Na bonds. This may be due to the difference between the electronegativities of vanadium and sodium ions. As a result, addition of sodium ions suppresses Lewis acidity and simultaneously Brønsted acidity is also suppressed.

Photooxidation of 2-Propanol

It has been proposed that photooxidation of a secondary alcohol on TiO_2, proceeds via two reaction paths: (i) oxidative dehydrogenation to form a ketone, and (ii) oxidation of corresponding alkene formed by dehydration (*12*). According to this mechanism, propanone would be formed via both paths (i) and (ii), and ethanol via path (ii) from 2-propanol. In the present case, however, path (ii) is not acceptable because (1) no trace of acraldehyde, which is one of the main products of propene photooxidation, was detected; (2) the amount of ethanal produced was almost proportional to that of propanone produced on each catalyst, while ethanal formation from propene was suppressed with the amount of added sodium ions; and (3) there was no evidence of an enhancement of dehydration of 2-propanol by the photoirradiation (dehydration is rather supposed to be a thermal reaction). Hence, we propose that a common intermediate is formed at first and parallel reactions (C–H and C–C bond fissions) from the intermediate lead to propanone and ethanal as indicted in Scheme 3.

Proportional relation of the yields of propanone and ethanal over each catalyst indicates that the probability of bond fission is constant over each catalyst. This suggests that the addition of sodium ions does not affect the bond-fission steps. Table 3 shows the yields of propanone and ethanal normalized to $R_{V=O}$ values. Except for the case of VSS5, they are not very different from each other. Although the number of photoinactive V=O species may be included in $R_{V=O}$, the results listed in Table 3 strongly suggest that the activity of an active site is not affected by the addition of sodium ions.

Photooxidation of Propene

In contrast to the results of the photooxidation of 2-propanol, the selectivity of the two main products, acraldehyde and ethanal, varied significantly by addition of sodium ions. The dependence of the acraldehyde yield upon the Na_2O content is similar to that of propanone and ethanal from 2-propanol. On the other hand, the yield of ethanal decreases monotonically with an increase in the amount of sodium ions. This parallels the acidic property of the catalyst presented by the ratio of [propene]/[unreacted 2-propanol] in Table 1. The difference in the yields of ethanal and acraldehyde in the photooxidation of propene reflects the difference of their reaction pathways as reported previously (*4*); C=C fission leads to ethanal formation and ab-

TABLE 3

Normalized Yields of the Products in Photooxidation of 2-Propanol

Catalyst	$R_{V=O}$	Normalized yield (μmol)	
		CH_3COCH_3	CH_3CHO
VS	0.48	26.0	0.7
VSS01	0.51	31.0	0.7
VSS1	0.70	29.1	0.6
VSS2	0.59	27.8	0.6
VSS5	0.29	11.0	—

Note. $R_{V=O}$: see text. The yields listed in Table 1 are normalized to $R_{V=O}$.

straction of hydrogen leads to acraldehyde. Ai (*24*) correlated the selectivity of C=C bond fission of and hydrogen abstraction from *cis*-2-butene to the acidic and basic properties of the vanadia-based catalysts. He found that in the case of a highly acidic catalyst, C=C bond fission to form ethanoic acid was promoted, whereas in the case of a basic catalyst hydrogen abstraction to form maleic anhydride was promoted. This finding is very suggestive for the present result although our reaction includes photo processes.

Such common phenomena between photo and thermal catalysis suggest that acidity may be one of the factors governing photocatalysis.

Surface Vanadates

From the UVS results it is concluded that at least three vanadates are present on the surface of VS. Comparison of these three vanadates varies with the amount of added sodium ions. Although a change in the reactivity of the catalyst by addition of sodium ions may seem to be caused by the formation of new kinds of surface species, the UVS results suggest that the sodium ion addition does not bring about the formation of new surface species but only controls the composition of the surface vanadates. Thus the appropriate addition of sodium ions brings about the preferential formation of the active species which has the absorption band centered at 315 nm. This band observed on the silica-supported catalyst has already been assigned to the oxygen-to-vanadium charge-transfer transition of VO_4 tetrahedra by Kazansky *et al.* (*25, 26*), by the combined use of UVS and photoluminescence techniques, as shown by

$$V^{5+}{=}O^{2-} \underset{-h\nu'}{\overset{+h\nu}{\rightleftharpoons}} (V^{4+}{-}O^{-})^{*} \qquad (1)$$

The other bands, A_v and A_{260}, may relate to inactive and/or less active species. Band A_v is assignable to aggregated vanadates as mentioned above. There have been many reports which point out that aggregation of vanadates occurs easily on silica (*27–30*) since the affinity of vanadium oxide to silica is not strong. In these reports, it is thought that even at a low level of loading of vanadium oxide (~5 wt%), a major part of the vanadates is stabilized as a polymeric phase. In polymerized vanadates, even if a (V=O) bond exhibiting band A_{315} were present, the excited electron and hole generated by Eq. (1) would tend to be delocalized and deactivation would occur quickly. V_2O_5 is known to be photoinactive (*7*).

The other band A_{260} is probably due to an inert phase. For comparison of the surface vanadates, UVS of γ-alumina-supported vanadium oxide (5 wt%), a photoinactive catalyst (*1*), is shown in Fig. 5. The spectra of the alumina-supported catalyst and VSS5 are almost identical. The presence of highly dispersed vanadates on the γ-alumina surface has been proposed by Echigoya *et al.* (*30*) from ESR spectra, by Roozeboom *et al.* (*31*) from Raman spectroscopic evidence, by Inomata *et al.* (*32*) from results on the NO–NH_3 reaction and other combined techniques, and by Kozłowski *et al.* (*33*) and us (*34*) from X-ray absorption spectra. Furthermore, the inert vanadates are proposed to have a tetrahedral structure (VO_4) (*31, 33, 34*). If the inert vanadate on alumina is the same as that of VSS5, two kinds of monomeric tetrahedral species should be present on the silica surface; one is photoactive and the other is photoinactive. Our recent result on the X-ray absorption spectrum of VSS5 catalyst (*35*) supports the view that the major part of the vanadates of VSS5 is the monomeric tetrahedral species, indicating that the vanadium oxide of VSS5 is highly dispersed. Nevertheless, the low $R_{V=O}$ of the catalysts at high Na_2O contents suggests that the inactive tetrahedral species may also be inactive against oxygen exchange with propanone. The increase in the ratio of the inert vanadate results in a decrease in $R_{V=O}$, as seen in the case of catalysts containing more than 1.9 wt% Na_2O. The inert vanadate may be stabilized in a cage of the support or sodium oxide.

In summary, the addition of sodium ions affects the local structure of vanadate species as follows. In sodium-ion-free catalyst (VS), three kinds of vanadates (polymerized phase, monomeric active phase, and monomeric inactive phase) are present. The addition of sodium ions tends to decrease the concentration of the polymeric phase, resulting in an increase in the monomeric phase and the enhancement of the activity. The fraction of the active phase is maximized in the vicinity of 1 wt% Na_2O. At higher Na_2O contents, the monomeric active phase gradually changes to the monomeric inactive phase, and consequently the VSS catalyst becomes less active than VS.

The local structure of vanadates is considered to be controlled essentially by the pH values of the solution used for impregnation of the silica. In a highly alkaline region ($pH > 13$), vanadates are present as a mononuclear species like VO_4^{3-} and the ions become aggregated gradually with reduction of the pH, finally becoming a decavanadate ion under acidic conditions (*36*). The ordinary supported catalysts are usually prepared by impregnation with neutral or acidic solutions, while in preparing VSS a strongly basic solution was used. This is probably the main reason why monomeric VO_4 were preferentially formed by addition of sodium ions. Thus, a sodium ion works as a reagent to make a solution for impregnation strongly basic to form monomeric vanadate ions and also to neutralize the surface acidity of the calcined catalysts.

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