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Surface States of Titania(Rutile and Anatase)-Supported Vanadium Oxide Catalysts as Prepared by a Column-Exchange Adsorption Method and Their Catalytic Features

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Monolayer or less monolayer vanadium oxide catalysts supported on TiO_2(rutile and anatase), V_2O_5/R- and A-TiO_2, were prepared by a "column-exchange adsorption" method such as passing an oxovanadium ion solution, the pH of which was adjusted at 2, 4, and 7, through a column packed with titania (TiO_2) for impregnation. V_2O_5/R-TiO_2 pretreated at 450 °C showed an ESR spectrum with an unresoluved hfs for V(IV) ions at 77 K without depending upon the pH upon impregnation. V_2O_5/A-TiO_2 pretreated at room temperature showed quite small ESR signals due to Ti(III) and V(IV) ions. These signals tended to be intensive with increasing pH upon impregnation. After a heat treatment at 400 °C a huge and quite broad spectrum, which was ascribed to some reduced vanadia species($V_2O_{5-\delta}$), appeared in addition to the spectra for the Ti(III) and V(IV) ions, while such a change was never found in V_2O_5/R-TiO_2. Based on a theoretical treatment for the *g*-values, V(IV) ions on V_2O_5/R-TiO_2 have been confirmed to be replaced just into Ti ion sites on rutile(almost D_{2h} symmetry). With V_2O_5/A-TiO_2, V(IV) ions were shown to be placed so as to be partially subject to an anatase surface field(almost D_{2d} symmetry); that is, to be placed only near the vacant Ti ion site on anatase. From a comparison of the hf-coupling constant the vanadia species on rutile was clearly shown to interact more strongly with the surface than that on anatase. The 2-propanol decomposition rates over the catalysts were measured in the temperature range 270—350 °C as a test reaction. The activity of V_2O_5/R-TiO_2 was generally higher than that of V_2O_5/A-TiO_2. The lowest activation energy was obtained upon the impregnation at pH=2 for V_2O_5/R-TiO_2 and at pH=7 for V_2O_5/A-TiO_2. The best catalyst was not necessarily prepared through conditions with pH=4, which had been suggested as giving an effective monolayer-vanadia species.

Supported vanadium oxide catalysts have been widely used for the selective oxidation of hydrocarbons. They are usually prepared by the impregnation of oxovanadium ions on carriers; e.g., from aqueous solutions of NH_4VO_3,[1-3] oxalic acid solutions of NH_4VO_3[4] and V_2O_5,[5] and $VOSO_4$ aqueous solutions.[6] Their deposited states have been favorably investigated by analyzing ESR spectra for the V(IV) ion as a probe.[1-4,7,8] Roozeboom et al.[9-11] suggested that the so-called monolayer vanadium oxide catalyst could be favorably prepared by the impregnation of oxovanadium ions at a controlled pH of 4, since the oxovanadium ion has been known to be in such a polymerized state as decavanadate ion at pH=3—4 in aqueous solution.[12] Such a trial has already been reported by Sonnemans and Mars for the preparation of an alumina-supported MoO_3 catalyst[13] They showed that a vanadium oxide monolayer catalyst supported on titania(a mixture of rutile and anatase) is significantly active for methanol oxidation to formaldehyde.[11] Recently, many investigators have reported that "monolayered" vanadia deposited on titania, especially on anatase, has an excellent selectivity for the oxidation of hydrocarbons. They have discussed variously its deposited or interacting states according to ESR data, laser Raman spectroscopy, XPS, and TPD.[14-16] We have been interested in why such a supperior selectivity arises from the vanadia–titania system, especially from such monolayer vanadia on anatase. With respect to a rutile supported vanadia catalyst, which was prepared according to Roozeboom et al.,[9] we analyzed the deposited state of the vanadia species by ESR spectrometry and confirmed that the vanadia species dispersed quite homogeneously over the surface and that vanadium ions replaced mainly the surface Ti ion sites.[17]

In the present study, in order to make clear whether or not such pH-control upon impregnation is really effective, we prepared titania(rutile and anatase)-supported vanadium oxide catalysts by impregnation at different pH(=2, 4, and 7) and investigated their deposited states by ESR and their catalytic activitis for 2-propanol decomposition as a test reaction. In this paper we also discuss how the difference in the morphorogy of the carriers, rutile and anatase, affects the deposited state and catalytic features.

Experimental

1) Materials and Preparation Procedures. Anatase(A-TiO_2 Kanto Chem. Co. Ltd., guaranteed grade) were pulverised with an agate mortar and sieved between 100 and 170 meshes. Rutile(R-TiO_2), which was prepared from the anatase by heat treatment at 100 °C for 3 h, was pulverized and sieved between 100 and 170 meshes. V_2O_5 powder was prepared by the thermal decomposition of NH_4VO_3(Wako Pure Chem. Co. Ltd., guaranteed grade) in an air stream at 600 °C for 3 h for use as a reference catalyst.

7.9 grams of Sample R-TiO_2 was packed into a glass column (O.D.=15 mm), the length of which was about

75 mm. About 0.5 wt% of NH_4VO_3(Kanto Chem. Co. Ltd., guaranteed grade) aqueous solutions, the pH of which were exactly adjusted to 2, 4, and 7 by adding HNO_3 and NH_4OH, were poured into the column in order to cause the oxovanadium ion to be adsorbed. Each 3 ml of the effluent solution was collected in order to trace any changes in the pH and the concentration of vanadium ion while passing through the column. The effluent speed was about 0.1 ml min^{-1}. In the case of Sample A-TiO_2, 7.2 g were packed into the column; the NH_4VO_3 solution was also poured until both the pH and the vanadium ion concentration had recovered just to the original values. The values were determined by the use of a pH meter, TOA(model HM-7B), and by the usual Mohr salt method, respectively. The R- and A-TiO_2 adsorbing oxovanadium ion were dried at 110 °C for 8 h, and then calcined at 400 °C for 2 h in order to prepare titania supported vanadium oxide catalysts, V_2O_5/R-TiO_2 and V_2O_5/A-TiO_2, respectively.

2) Measurements and Computer Simulation. The surface areas of V_2O_5/R-TiO_2 and A-TiO_2 were determined by the usual BET method; N_2 gas adsorption at 77 K is shown in the 2nd column of Table 1. The surface area of V_2O_5 powder was similarily determined to be 8.5 $m^2\,g^{-1}$. Those TiO_2 were identified by comparing their X-ray powder diffraction patterns with ASTM cards. The X-ray diffractometer used was a Rigagu Denki Model GF-Rad-γA; Cu $K\alpha$- radiation(40 kV and 120 mA) and a nickel filter were also used. The deposited states of vanadium oxides were examined by ESR spectrometry. The ESR spectrometer used was a Nippon Denshi Model JES-PE(X-band 9.3 GHz and 100 kHz modulation). Computer simulation of the ESR spectrum was performed using an IBM 4381 system (described in detail later). The catalytic activities for 2-propanol decomposition, as a test reaction, were measured by the use of a closed circulation system(ca. 0.5 dm^3) connected directly to a gas chromatgraphy system with a Porapac-Q column(1 m). 20 mg of the catalysts were widely spread on the bottom of the vessel and preheated at the reaction temperature in air for 1 h before the reaction. The vessel containing 2-propanol was cooled by an ice-water bath during the reaction in order to maintain the vapor pressure constant at 8.4 mmHg (1 mmHg=133.322 Pa). The amount of the main product, which was confirmed to be propylene, was measured at intervals of 2 min. The decomposition rates were determined from the amount produced during the initial 20 min. The reaction temperature was controlled within±0.5 °C in the range 270—350 °C.

Results

1) The Amounts of Vanadium Oxide Deposited on Rutile and Anatase. When about 0.5 wt% of an ammonium metavanadate solution was poured into a glass column packed with rutile(R-TiO_2), the pH and vanadium ion (V-ion) concentration of the effluent solution varied as shown in Fig. 1. The pH initially increased from 2 to 5.5 in a run of pH=2, and from 4 to about 6 in a run of pH=4; it decreased from 7 to near 6 for pH=7. Eventually, they all returned to their original values. The amounts of oxovanadium ion adsorbed on R-TiO_2 were evaluated according to the V-ion concentration vs. time-curve. The adsorbed amounts of oxovanadium ion, which was estimated under the assumption that it was deposited in the form of V_2O_5, are given in the 3rd and 4th column of Table 1 (in units of mg(V_2O_5)/g-carrier and mg-(V_2O_5)/m^2, respectively). The surface coverages are given in the 5th column of Table 1. They had been estimated under the assumptions that the V–O–V network of V_2O_5 extends two-dimensionally on the surface and that the V–O bond length is 2.0 Å.

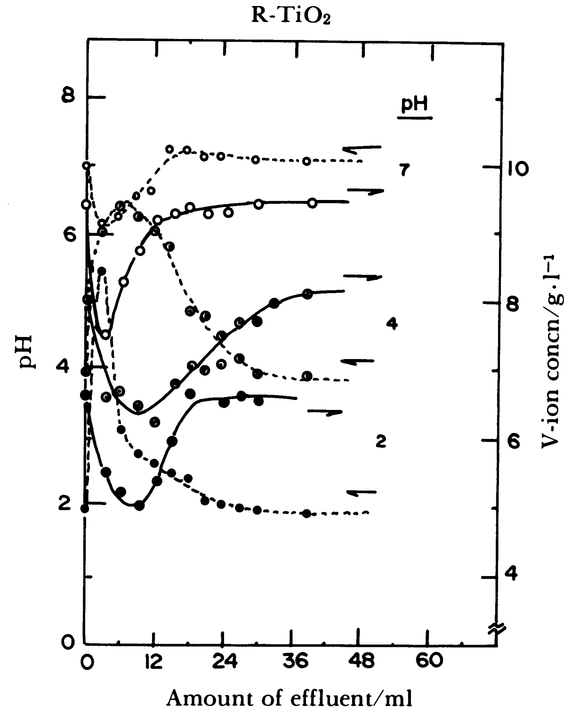

Fig. 1. The variations in the pH and the vanadium ion concentration of ammonium metavanadate solution during passing through the rutile-packed column. ----: pH changes and ——: V-ion concentration changes in the original solutions of pH=2, 4, and 7.

For A-TiO_2, the changes in the pH and the V-ion concentrations of the effluent solutions are shown in Fig. 2. The pH value initially increased in all cases and then gradually returned to the original values. The pH initially increased up to 7.5, even in the run for pH=7; this suggests that the A-TiO_2 has a weak basisity. The vanadium ion concentrations initially decreased and then recovered to the original values accompanied by pH changes. We similarly estimated the amount of vanadium oxide deposited (given in the 3rd and 4th columns of Table 1; the surface coverage is given in the 5th column).

2) ESR Spectra of V(IV) and Ti(III) Ions on R- and A-TiO_2-Supported Vanadium Oxide Catalysts. The spectrum for an R-TiO_2-supported vanadium oxide catalyst (V_2O_5/R-TiO_2) impregnated at pH=2 is illustrated in Fig. 3. This is the most clear spectrum among the catalysts impregnated at pH=2, 4, and 7,

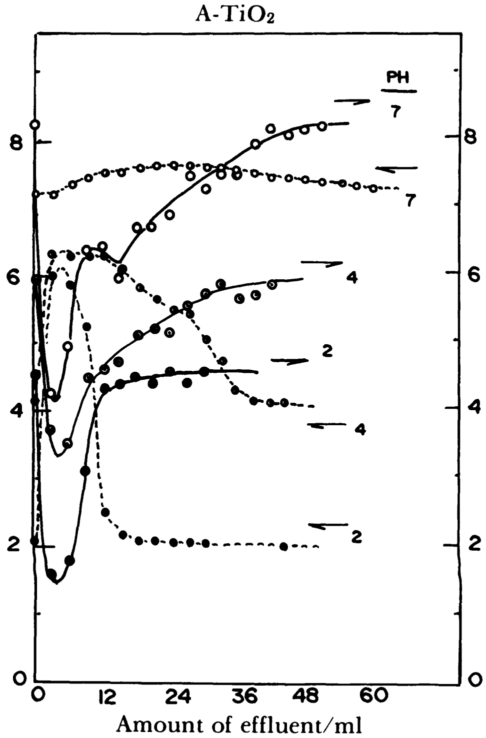

Fig. 2. The variations in the pH and the vanadium ion concentration of ammonium metavanadate solution during passing through the anatase-packed column. ----; pH changes and ——: V-ion concentration changes in the original solutions of pH=2, 4, and 7.

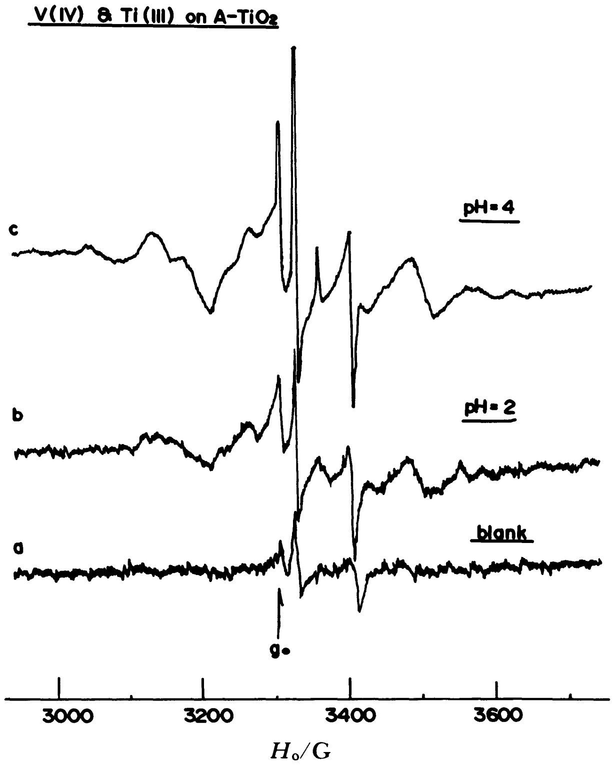

Fig. 4. The ESR spectra of anatase-carrier and V_2O_5/A-TiO_2 impregnated at pH=2 and 4, which were measured at 77 K after an evacuation at room temperature.

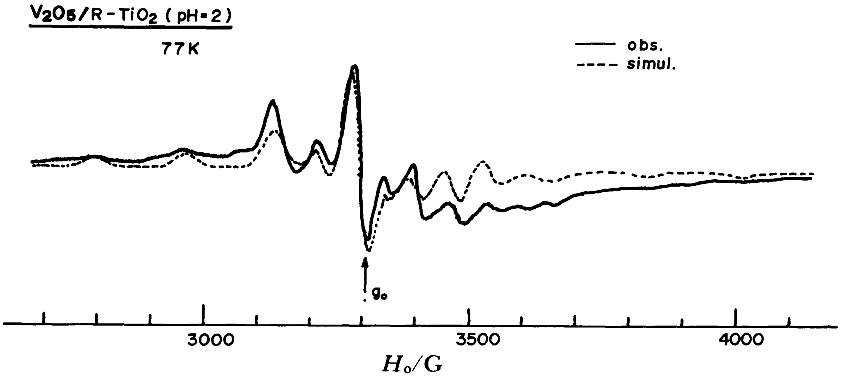

Fig. 3. The ESR spectrum for V_2O_5/R-TiO_2 and the best-fit spectrum previously simulated.[17] ——: observed and ----: simulated.

Table 1. Surface Areas of V_2O_5/R- and A-TiO_2 Catalysts, the Deposited Amounts of Vanadium Oxide (Reduced to V_2O_5), and the Surface Coverages

Catalyst	Surface area/$m^2 \cdot g^{-1}$	Deposited amount (V_2O_5) mg/g-carrier	Deposited amount (V_2O_5) $mg \cdot m^{-2}$	Surface coverage θ
R-TiO_2-carrier	2	—	—	—
V_2O_5/R-TiO_2 (pH=2)	2	2.66	1.30	0.66
V_2O_5/R-TiO_2 (pH=4)	2	4.88	2.44	1.2
V_2O_5/R-TiO_2 (pH=7)	2	1.81	0.90	0.47
A-TiO_2-carrier	8.5	—	—	—
V_2O_5/A-TiO_2 (pH=2)	6.7	3.2	0.48	0.25
V_2O_5/A-TiO_2 (pH=4)	6.4	6.6	1.03	0.53
V_2O_5/A-TiO_2 (pH=7)	6.5	10.2	1.57	0.82
V_2O_5-powder	8.5	—	—	—

which have been observed at 77 K after evacuation at 470 °C for 1 h. The spectrum had been regarded as containing poorly resolved hfs of vanadium(^{51}V) nucleus(I=7/2).[17] The result of a computer simulation is given along with a broken line in Fig. 3; the best-fit parameters used are given in Table 2. The spectrum was assigned to the V(IV) ion substituting the titanium ion site on the rutile surface.[17] V_2O_5/R-TiO_2 prepared at the other pH(=4 and 7) gave a similar spectrum, although the intensity was relatively low; thus, the spectrum could not be clearly observed.

An A-TiO_2 carrier, itself, gives a very weak signal due to Ti(III) ions. The intensity, however, became intensive along with the deposition of vanadium oxide. The ESR spectra for an A-TiO_2-supported vanadium oxide catalyst(V_2O_5/A-TiO_2) prepared at 2, 4, and 7 are illustrated in Figs. 4-b, c and 5-C. They

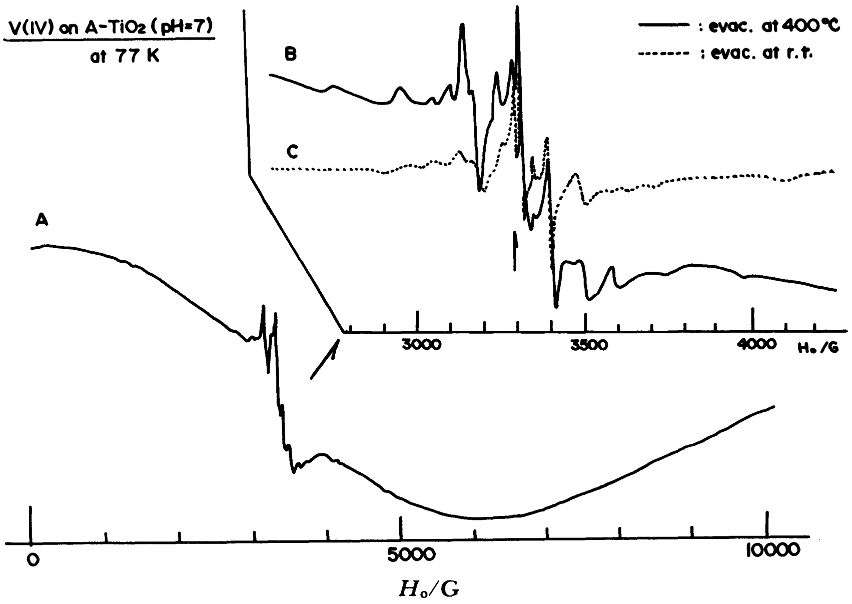

Fig. 5. The ESR spectrum of V_2O_5/A-TiO_2 impregnated at pH=7: Spectrum A indicates the wide range spectrum from zero to 10000 G, measured at 77 K after the evacuation at 400 °C: Spectrum B is the spectrum A that was recorded in the field between 2600 and 4200 G in order to show clearly the signal corresponding to the V(IV) and Ti(III) ions: Spectrum C the spectrum that was recorded in the field between 2600 and 4200 G at 77 K after the evacuation at room temperature.

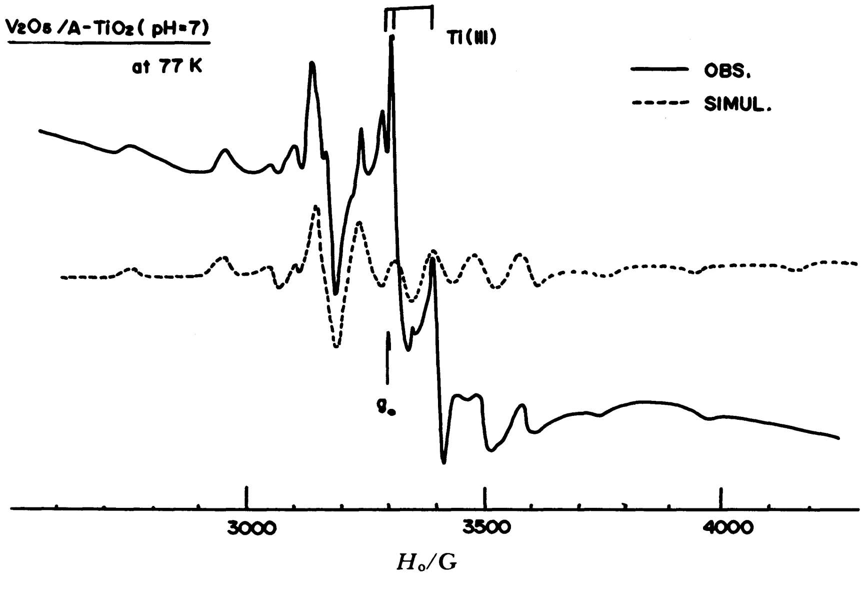

Fig. 6. The observed spectrum for V(IV) ion on V_2O_5/A-TiO_2(pH=7) and the best-fit spectrum simulated. ——: observed and ----: simulated.

were measured at 77 K after evacuation at room temperature for 1 h. The signal intensities for Ti(III) and V(IV) ions tends to increase simulteneously as the pH upon impregnation becomes high (pH=2→7). This change corresponds well to the surface coverage of the vanadia species (Table 1). When V_2O_5/A-TiO_2 was pretreated at 400 °C for 1 h, the spectrum varied greatly: A very large, broad signal appeared and the unresolved hf-lines ascribed to the V(IV) ion became more clear, while the intensity of the signal corresponding to Ti(III) ion almost didn't change (Figs. 5-A and B). We applied a computer simulation to the component of the V(IV) ion in Fig. 5-B. The first derivative curve was calculated according to the usual simulation method[18,19] at intervals of 10 G (1G=10^{-4} T) in a magnetic field of 2500—4300 G (as described previously[17]). The intensity of the microwave absorption at each resonance field was obtained by numerical integrations at intervals of 1.5° to θ and ϕ for all directions under the assumption of a Gaussian shape function and 35 G of the half width. The best-fit parameters are given in Table 2 and the simulated spectrum for the V(IV) component is indicated by the broken line in Fig. 6. The g-tensor for the Ti(III) ion(Fig. 6) was estimated as $g_{/\!/}$=1.94 and $g_\perp$=2.00 and 1.99 (Table 2).

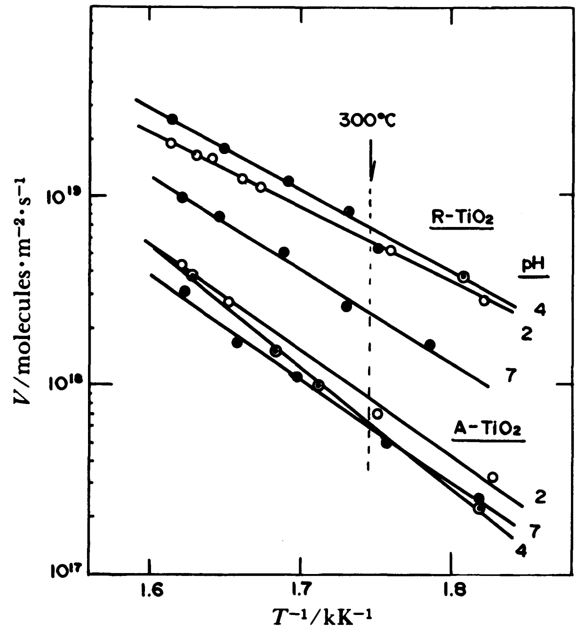

Fig. 7. Arrhenius plots of the 2-propanol decomposition rates over V_2O_5/R- and A-TiO_2 impregnated at various pH.

3) Decomposition Rates of 2-Propanol over V_2O_5/R-TiO_2 and A-TiO_2. The rates of 2-propanol decomposition over titania-supported vanadium oxide catalysts were determined from changes in the GC-peak intensity for the produced propylene in the temperature range 270—350 °C. Arrhenius plots for the initial mean rates, thus obtained, are summarized in Fig. 7. Arrhenius parameters, log V_o and E_a, estimated from those plots, are given in Table 3. The minimum activation energy was obtained as 18.1 kcal mol^{-1} (1cal=4.184 J) for V_2O_5/R-TiO_2 prepared at pH=2, while the maximum as 29.6 kcal mol^{-1} for V_2O_5/A-TiO_2 prepared at pH=4. With respect to V_2O_5/R-TiO_2 the higher the pH upon impregnation, the larger the E_a. With V_2O_5/A-TiO_2, the catalyst prepared at pH=7 gives a minimum activation energy and that at pH=4 a maximum. The decomposition rate at 300 °C estimated with units of molecules/m^{2}s and molecules/mg(V_2O_5)s, are summarized in Figs. 8 and 9, respectively. The reaction rates over a V_2O_5 powder and the carrier, themselves(Blank), were added

Table 2. The Best Fitting Parameters Used for the Simulation of ESR Spectra of V(IV) Ion in V_2O_5/R- and A-TiO_2 Catalysts Evacuated at 400°C

Catalyst	Species	g-value		A-value	
		$g_{/\!/}$	$g_\perp$	$A_{/\!/}$	$A_\perp$
V_2O_5/R-TiO_2	V(IV)	1.950	1.983	173.1	55
V_2O_5/A-TiO_2	V(IV)	1.912	1.981	200	75
V_2O_5/A-TiO_2	Ti(III)	1.94	1.99 2.00	—	—

Table 3. Arrhenius Parameters of 2-Propanol Decomposition over V_2O_5/R- and A-TiO_2 Catalysts Impregnated at pH=2, 4, and 7

Catalyst	log V_o/molecules·m^{-2}·s^{-1}	E_a/kcal mol^{-1}
V_2O_5/R-TiO_2 (pH=2)	25.6	18.1
V_2O_5/R-TiO_2 (pH=4)	26.5	20.3
V_2O_5/R-TiO_2 (pH=7)	27.1	23.0
V_2O_5/A-TiO_2 (pH=2)	27.8	26.0
V_2O_5/A-TiO_2 (pH=4)	29.0	29.6
V_2O_5/A-TiO_2 (pH=7)	27.3	25.1

in Figs. 8 and 9 for a comparison. The activity of V_2O_5/R-TiO_2, per m^2s, is 3—10 times higher than that of the carrier itself; also, the activity of V_2O_5/A-TiO_2 is about 3—4 times higher than that of the carrier itself. In both V_2O_5/R-TiO_2 and A-TiO_2 catalysts the activity, per mg(V_2O_5)s, became maximum upon impregnation at pH=2; further, those values are 50—130 times higher than that of V_2O_5 powder. Thus, it is evident that vanadium oxide is very effectively dispersed on the titania, especially on rutile impregnated at pH=2.

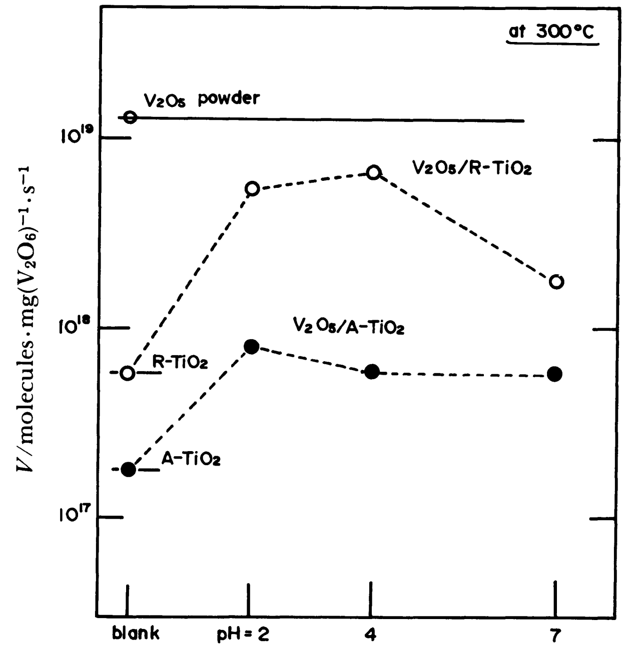

Fig. 8. Comparison of the activity(molecules/m^2 s) for 2-propanol decomposition among V_2O_5 powder, the carrier themselves, and the supported vanadium oxide catalysts at 300 °C.

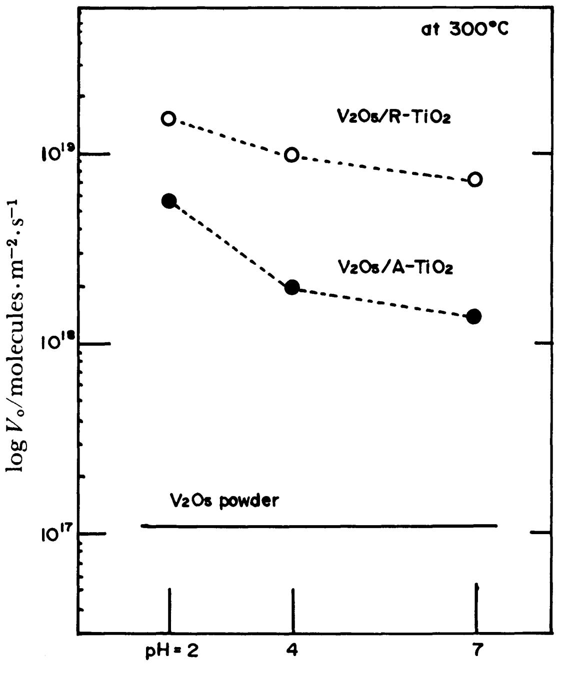

Fig. 9. Comparison of the activity(molecules/mg(V_2O_5)s) among the V_2O_5 powder and the supported catalysts at 300 °C.

Discussion

Deposited States of Vanadium Oxide on TiO_2-(Rutile and Anatase). Shimizu[20] has strictly investigated the relationship between the g-tensor and the crystal field splitting of the d-orbital for V(IV) ions doped in a TiO_2(rutile) single crystal subject to a D_{2h} symmetry field. We successfully applied the theory to an analysis of V(IV) ions placed into a V_2O_5 single crystal and subjected to the field of a distorted square pyramid.[21] Furthermore, the field symmetry around the V(IV) ions on rutile(V_2O_5/R-TiO_2) was clearly shown to be quite similar with that around V(IV) in the V_2O_5 single crystal.[17]

The anatase structure belong to the tetragonal symmetry of the space group $I4_1$/amd and the Ti ion is in a distorted oxygen octahedra of the symmetry group D_{2d}:[22] Qualitatively oxygen ions placed on square corners of an octahedra deviate a little (althernatively up and down from the plane[23] accompanied by a transition of rutile to anatase) as the coordination model in Figs. 10-(a) and (b) shows. The relationship between the g-tensor and the crystal field splitting for d^1-metal placed in a tetragonal field (D_{4h} symmetry) and in a slightly distorted tetragonal field, e.g., rohmbic and trigonal distortions,[24,25] is given approximately as

$$g_{/\!/} = g_0 - 8\lambda/\Delta \text{ and } g_\perp = g_0 - 2\lambda/\delta, \qquad (1)$$

where Δ and δ are the crystal field splitting constants

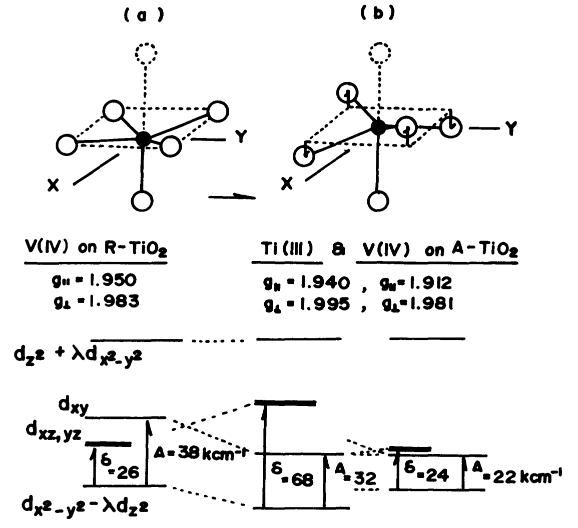

Fig. 10 Coordination model and crystal field splitting for the surface V(IV) ion in V_2O_5/R-TiO_2 and V_2O_5/A-TiO_2.

and λ the spin-orbit coupling constant (reasonably assumed to be 250 cm^{-1} [26]). If such a symmetry change as $D_{2h} \rightarrow D_{2d}$ accompanied by the transition, rutile→ anatase, is not too large for the application of the theory to the present system, we can similarly estimate the field splitting around V(IV) ion on V_2O_5/A-TiO_2. Such a deviation of the oxygen ions should directly cause the d_{xy}-level to be lower and the $d_{x^2-y^2}$ to be lower to some extnet; however, the d_{xz} and d_{yz} increase to some extent. The field splitting around the Ti(III) ion, which was estimated by appling Eq. 1 to the g-value in Table 2, agrees well with the expected value, as shown in Fig. 10-(b). With the V(IV) ion the d_{xy}-level decreased considerably, but the degree of the increase in the d_{xz}- and d_{yz}-levels and the decrease in the $d_{x^2-y^2}$ are not as large as expected (Fig. 10-(b)). The energy diagram suggests that the V(IV) ion is partially subjected to a symmetry field of the anatase surface; therefore, it may be placed only near a vacant Ti site on the anatase surface. Since both λ/Δ and λ/δ were less than 0.1 in the present estimation,[26] this theory could reasonably well be applied to this system.

Wacks et al.[16] suggested that two types of vanadia species were present on anatase deposited with V_2O_5: A surface vanadia species coordinated to the anatase and the crystallites of V_2O_5. In V_2O_5/TiO_2(anatase) with 2% or less V_2O_5, a monolayer of surface vanadia species was formed without any crystallite V_2O_5. Inomata et al.[27] observed the same ESR spectrum with unresolved hfs for a multilayered vanadium oxide deposited on rutile and anatase. They indicated that the g-value, $\langle g \rangle = 1.971$, was close to that in the V_2O_5 matrix. The present g-value corresponds well to that reported by Akimoto et al.[28] The present samples show almost the same extent of deposition with the monolayer or the less monolayer catalysts of Wacks et al.;[16] therefore, the deposited state is comparable with them. According to an FT-IR study by Miyata et al.,[29] the V=0 stretching band for the vanadia species on a less monolayer V_2O_5/anatase catalyst was found at 983 cm^{-1}. Kozlowski et al.[30] found by EXAFS and XANES measurements that a vanadium monolayer supported on anatase did not have the structural characteristics of crystalline V_2O_5 and suggested that the basic unit was a species with two terminal and two bridging bonds. The V(IV) ion placed near the site (expected by the coordination model in Fig. 10-(b)) may correspond to all these vanadia species. It was clearly mentioned in the discussion that the vanadia species were strongly affected by the surface field symmetry of the carrier; it was further suggested that V(IV) ions were placed just in and near the titanium ion vacant sites on rutile and anatase surfaces (cf. Figs. 10-(a) and (b), respectively. However, such models express only one of the possible deposited states and, of course, the possibility of a topochemical deposition of vanadium oxide just on the titania surfaces would not be ruled out.

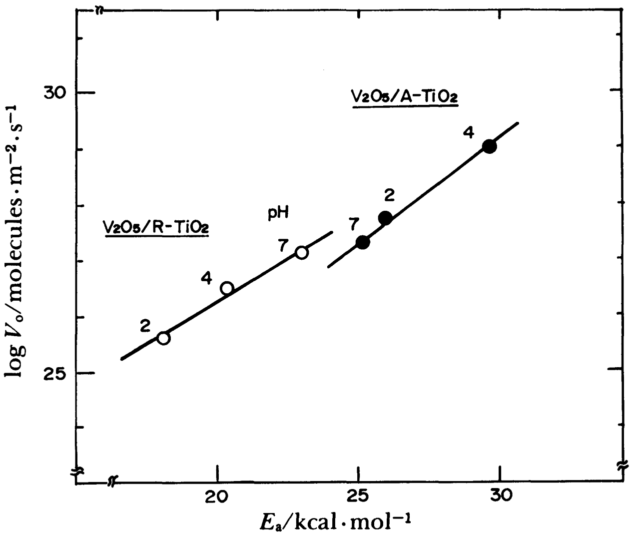

Fig. 11. Relationship between the pre-exponential factor(log V_o) and the activation energy(E_a) for 2-propanol decomposition over the titania supported vanadium oxide catalysts.

A huge ESR signal that appeared in V_2O_5/A-TiO_2 upon evacuation at 400 °C(Fig. 5) might have been due to a kind of dipole–dipole interaction between the V(IV) ions or to a triplet state of the V(III) ion. Reduced vanadia species were easily formed on an anatase supported vanadia catalyst, as also indicated by other authors.[15,16] Thus, the huge and broad ESR signal might be ascribed to some kind of reduced vanadia species that were placed in a micropore and were inhomogeneously dispersed on the anatase surface.

V_2O_5/R-TiO_2 showed a sharp ESR signal, which was assigned to the V(IV) ion, weakly interacting with the remaining oxygen molecules, upon evacuation at room temperature. No reduced type of spectrum was formed upon evacuation at 470 °C; only a simple spectrum with broad hfs for V(IV) ions has already been reported.[17] The hf-coupling constants($A_{/\!/}$ and $A_{\perp}$) are considerably larger in V_2O_5/A-TiO_2 than V_2O_5/R-TiO_2, as shown in Table 2. This suggests that the unpaired electron is located to a much greater extent on V_2O_5/A-TiO_2 than V_2O_5/R-TiO_2; thus, the vanadia species interacts more weakly with anatase than the rutile surface. This may correspond to the suggestion by Kozlowski et al.[30] that differences occur in the structure of the active phase when supported on different materials.

Catalytic Properties of V_2O_5/R-TiO_2 and A-TiO_2. Previously, we found a kinetic compensation effect for alcohol decomposition over alkali-modified vanadium oxide catalysts for successfully analyzing its activated states.[31] In the activated state of an alcohol molecule the internal frictional rotation of the alkyl group, especially the methyl group, has been insisted as being an important parameter. A compensation relation holds well between log V_0 and E_a for catalysts impregnated at different pH(=2, 4, and 7) in Table 3, as shown in Fig. 11. A desired catalyst should be located(relatively) on the left-hand side and on the upperpart of log V_0 vs. E_a-plots. From this point of view V_2O_5/R-TiO_2 is more desirable than V_2O_5/A-TiO_2, as can be clearly seen by comparing Figs. 8 and 9. Furthermore, with V_2O_5/R-TiO_2 the lowest activation energy was obtained upon impregnation at pH=2 and with V_2O_5/A-TiO_2 upon that at pH=7 instead of pH=4. Therefore, we could not find any special ability in catalysts prepared by impregnation at pH=4 (reported by Roozeboom et al. for preparation of a monolayer catalyst[9]). Through kinetic consideration, however, not only the kind of carrier but also the pH upon impregnation could be clearly demonstrated to delicately affect the deposit state of vanadia species, although ESR measurements have never detected such difference with the pH.

Many investigators have shown that monolayer vanadia species supported on TiO_2, especially on anatase, are superior catalysts for oxidation of *o*-xylene.[14–16] V_2O_5/A-TiO_2 seems to be considerably reduced during 2-propanol decomposition, while being kept in an oxidative state during the oxidation reaction. This means that the catalytic feature for 2-propanol decomposition can not be compared simply with that for oxidation. We will not discuss further their abilities as oxidation catalysts in the present paper.

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