JOURNAL OF CATALYSIS 34, 345–355 (1974)

The Structure and the Activity of Vanadyl Phosphate Catalysts

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Received November 26, 1973; revised April 11, 1974

Vanadyl phosphate catalysts with a variety of phosphorus content and a variety of degree of aggregation of vanadium ions were prepared. It was found that the selectivity and the activity of the catalysts for the synthesis of maleic anhydride from butene-1 are closely related to the oxidation number and the degree of aggregation of vanadium ions. Vanadyl phosphate catalysts in which V:P = 1:2, and the average oxidation number of vanadium ions is 4.0, and vanadium ions are highly aggregated, gave high selectivity. The catalytic reactions seem to proceed through V^{4+}–V^{5+} redox mechanism in which V=O bonds play an important role.

INTRODUCTION

Vanadyl phosphate catalysts (VP catalysts) have been used for the production of maleic anhydride from butene (*1*). The structure and the activity of V_2O_5–P_2O_5 catalysts prepared by melting the mixtures of vanadium pentoxide and phosphorus pentoxide have been investigated by Yoshida and co-workers (*2*), and an important role of V=O bond in their catalytic activity has been pointed out. However, the structure of VP catalysts prepared from aqueous solutions of VO^{2+} ions and phosphoric acid has not been reported yet in spite of their importance as industrial catalysts. In the present study, the structures of VP catalysts prepared from aqueous solutions were investigated by using an X-ray fluorescence analyzer, an X-ray diffractometer, an ir spectrophotometer, an ESR spectrometer, a magnetic balance, polarography, and chemical analysis. The relation between the structure and the activity of these catalysts is discussed.

EXPERIMENTAL METHODS

Preparation of Catalysts

VP catalysts supported on alumina were prepared as follows: 0.0128 mole of ammonium metavanadate and 0.0256 mole of reducing agent were dissolved in 50 ml of water, and warmed to obtain a blue solution of VO^{2+} ions. Then phosphoric acid was added to this solution, followed by the addition of 12 g of alumina carrier, and water was evaporated on a water bath. Supported catalysts thus obtained were dried at 100°C for 4 hr, and calcined at 400°C for 2 hr in an electric furnace.

Alumina carrier was obtained by calcining Neobead-C (Mizusawa Chemical Co.), which is a spherical alumina gel of about 3 mm diameter, at 1300°C for 3 hr. The alumina carrier thus obtained was α-alumina with pore volume and surface area of 0.25 ml/g and 5.0 m^2/g, respectively. This carrier has sharp pore radius distribution, and its average pore radius was 1100 Å.

Unsupported VP catalysts were prepared by drying the solutions of VO^{2+} ions and phosphoric acid, and by calcining the dried materials at 400°C for 2 hr.

As reducing agents of ammonium metavanadate, oxalic acid (OA), *d,l*-malic acid (MA), citric acid (CA), and *d*(L)-tartaric acid (TA) were used; and in this paper the VP catalysts obtained by using these reducing agents are called OA-VP, MA-VP, CA-VP, and TA-VP, respectively. In some cases the last three catalysts are called hydroxy carboxylic acid VP catalysts (HCA-VP).

Measurements

Atomic ratios of V:P for unsupported OA-VP's were measured by X-ray fluorescence analysis, with a Rigaku Denki Geigerflex 3063-3A analyzer, by using mechanical mixtures of ammonium metavanadate and diammonium hydrogen phosphate as standard samples. For other VP catalysts, atomic ratios of V:P were not measured, but the mole ratios of ammonium metavanadate to phosphoric acid used in their preparation were used instead of true V:P ratios.

X-Ray diffraction diagrams were obtained with a Rigaku Denki Geigerflex D-3F diffractometer, with Cu $K\alpha$ radiation.

Infrared spectra were obtained by KBr disk technique with a JASCO DS-403G spectrophotometer.

Measurements of ESR spectra were made at room temperature on a JEOL-ME spectrometer, with X-band frequency using 100 kc modulation with the modulation width of 5 G, and using Mn^{2+}/MgO as the standard of static magnetic field. ESR parameters such as g values, hyperfine coupling constants, and line widths were determined by fitting the calculated spectra to the observed ones. A computor program was made in order to calculate the line shape of isotropic or anisotropic ESR spectra with axial g and A tensors with Gaussian or Lorentzian line shape. The magnetic field corresponding to six resonance lines for Mn^{2+}/MgO was also calculated, and the six resonance lines as well as the calculated spectrum were plotted on a Iwasaki Tsushin DTL-602 digital plotter. Calculations of ESR line shapes were made with a JEOL JES-6 spectrum computor.

Magnetic susceptibilities were measured by Gouy method at magnetic field of about 13000 G at room temperature by using purified water as a standard sample.

The average oxidation numbers of vanadium ions in VP catalysts were determined by redox titration as follows: 0.1–0.2 g of unsupported or about 1 g of supported catalyst was dissolved in the mixture of 10 ml of 18 N sulfuric acid and 4 ml of 46% hydrofluoric acid. This solution was poured into 250 ml of water in which 10 ml of saturated boric acid and 10 ml of 18 N sulfuric acid had been added in advance. Oxidation titration of this solution was carried out with 0.1 N potassium permanganate. V^{3+} and V^{4+} ions are oxidized into V^{5+} ions by this treatment.

$$aV^{3+} + bV^{4+} + cV^{5+} - (2a + b)e^- \rightarrow (a + b + c)V^{5+}. \quad (1)$$

Then reduction titration was made with 0.1 N Mohr's salt using diphenyl amine dissolved in concd phosphoric acid as an indicator. V^{5+} ions are reduced into V^{4+} by this treatment.

$$(a + b + c)V^{5+} + (a + b + c)e^- \rightarrow (a + b + c)V^{4+}. \quad (2)$$

Thus average oxidation number of vanadium ions can be calculated by the following equation.

$$\text{Ox. No.} = \frac{3a + 4b + 5c}{a + b + c} = 5 - \frac{2a + b}{a + b + c} = 5 - \frac{N_o}{N_r}, \quad (3)$$

where N_o and N_r are the quantities of consumed potassium permanganate and Mohr's salt in gram equivalents, respectively.

Polarography measurements were carried out for solutions which were prepared by diluting the above mentioned hydrofluoric acid–sulfuric acid solutions of VP catalysts with the volume of water ten times as much as that of acid solutions.

Surface area of alumina carrier was measured by BET method, using nitrogen gas at liquid nitrogen temperature. Pore volume and pore radius distribution of alumina carrier were measured with Carbo Erbá Model 70 mercury pressure porosimeter.

Oxidation of Butene-1

The oxidation of butene-1 was carried out at atmospheric pressure by the conventional flow method using 10 ml of catalysts supported on alumina. The reaction was carried out at 400, 450, and 500°C for 2 hr at each temperature. The reacted gas was bubbled into water, and the yields of maleic anhydride and acetic acid were determined by measuring the NMR spectrum of this aqueous solution using dioxane as an internal standard of signal intensity. The conversion of butene-1 was determined by measuring the gas chromatograms of gases before and after the reaction.

EXPERIMENTAL RESULTS

1. Structures of OA-VP

Since OA-VP catalysts have been used industrially for the production of maleic anhydride from butene (*1*), the structures of these catalysts were investigated in some detail. In Table 1, components, colors, oxidation numbers of vanadium ions, magnetic susceptibilities, ESR parameters, and crystal structures of OA-VP's are tabulated.

X-Ray diffraction patterns for the sample of No. 1 ($f_p = 0.0$) and No. 2 ($f_p = 0.08$) agree with that for vanadium pentoxide. Here f_p is defined as the atomic ratio, P/(P + V). The sample of No. 3 ($f_p = 0.18$) gives diffraction lines at $2\theta =$ 20.2(15.5), 22.2(100.0), 26.4(9.5), 27.9 (78.5), 28.9(45.2), 33.4(14.3), and 35.9 (17.8), where the values in parentheses are relative heights of diffraction lines. This diffraction pattern has not been reported yet as far as we know. The samples with f_p larger than 0.27 (Nos. 4–9) do not show any diffraction lines, but give only one or two of broad and weak diffraction bands, indicating that these samples are in almost amorphous state.

Infrared spectra for these samples are shown in Fig. 1. The ir spectrum for No. 1 agrees with that for vanadium pentoxide as expected from its X-ray diffraction pattern. In this spectrum, peaks at 1015 and 825 cm^{-1} have been assigned to V=O stretching and V–O–V stretching vibrations, respectively (*3*, *4*). The sample of No. 2 gives similar spectrum, although V=O and V–O–V stretching vibrations are shifted to 995 and 855 cm^{-1}, respectively.

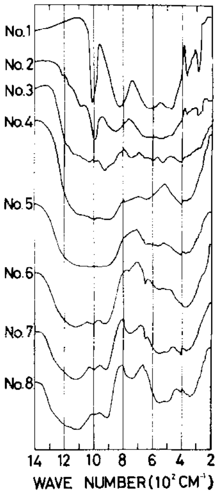

FIG. 1. Infrared spectra for various OA-VP samples.

Amorphous samples (Nos. 4–9) give

TABLE 1
SEVERAL PROPERTIES OF OXALIC ACID-VP CATALYSTS

Sample no.	f_p = P/(P + V)	Color	Av ox. no. of V	$\chi \times 10^6$	ESR parameters g value	 ΔH_{msl} (G)	Crystal structure
1	0.00	Orange	4.97	0.5	1.972	140	V_2O_5
2	0.08	Brown	4.98	0.4	—[a]		V_2O_5
3	0.18	Dark brown	3.97	13.6	1.961	310	Unknown
4	0.27	Black	4.33	8.4	1.959	300	Amorphous
5	0.36	Black	4.01	10.5	1.961	270	
6	0.48	Dark brown	3.97	8.1	1.960	360	
7	0.62	Grey	3.78	7.9	2.0[b]	1300	
8	0.75	Grey	3.40	8.8	2.0[b]	1400	
9	0.80	Yellow green	3.17	—	—[a]		

[a] $g_\parallel = 1.932$, $g_\perp = 1.980$, $A_\parallel = 205$ G, and $A_\perp = 75$ G.

[b] Too broad for g values to be determined precisely.

broad and simple bands at 800–1300 cm^{-1} region. In each of these spectra, an absorption band at about 1000 cm^{-1} is attributed to V=O stretching vibration, and a broad band at about 1000–1300 cm^{-1} to the stretching vibration of P–O bonds of phosphates (*5*). Absorption bands of P–O stretching vibration are known to appear at 1000–1060, 1060–1170, 1085–1250, and 1265–1300 cm^{-1} for ortho-, pyro-, tri-, and higher linear metaphosphates, respectively (*5*). Therefore the broadness of the P–O stretching vibration bands suggests that phosphoric ions have a variety of degree of condensation. From these spectra, it seems most likely that these amorphous VP catalysts are the complexes between vanadyl ions and condensed phosphoric ions. As mentioned below it is these amorphous catalysts that give maleic anhydride from butene with high selectivity. Therefore in what follows our main interest is confined to the structure and the catalytic activity of these amorphous catalysts.

Average oxidation numbers of vanadium ions in these catalysts are given in Table 1. The oxidation numbers of vanadium ions in the samples of Nos. 1 and 2 are almost 5.0 as expected from their crystal structures. The oxidation number of vanadium ions in No. 3, which is an unknown crystalline sample, is almost 4.0. The oxidation numbers for amorphous samples (Nos. 4–9) decrease gradually from 4.33 to 3.17 as f_p increases from 0.27 to 0.80. This fact indicates that vanadium ions of low oxidation numbers such as V^{4+} and V^{3+} are formed as the concentration of phosphoric ions increases.

The oxidation numbers measured by the present method are average oxidation numbers of vanadium ions. Therefore the quantity of each of V^{3+}, V^{4+}, and V^{5+} ions can not be directly determined by this method. However VP catalysts with average oxidation numbers between 3.0 and 4.0 (Nos. 3, 6, 7, 8, and 9) are considered to contain V^{4+} and V^{3+} ions and not V^{5+} ions, since V^{5+} ions could not be detected with polarography. Therefore for example, sample No. 7 in which average oxidation number of vanadium ions is 3.78 is considered to contain 78% of V^{4+} and 22% of V^{3+} ions. On the other hand, VP catalysts with the oxidation numbers larger than 4.0 (Nos. 1, 2, 4, and 5) are supposed to contain V^{4+} and V^{5+} ions and not V^{3+} ions, since these catalysts do not show the broadening of ESR spectra due to V^{3+} ions, as mentioned below. Thus for example, sample No. 4 (Ox. No. = 4.33) is considered to contain 33% of V^{5+} and 67% of V^{4+} ions.

ESR spectra for these VP catalysts are shown in Fig. 2. ESR parameters obtained from these spectra are given in Table 1. Amorphous samples with f_p from 0.27 to 0.75 (Nos. 4–8) give isotropic spectra with g values 1.960 ± 0.005. No. 9 gives a spectrum with well-resolved hyperfine lines due to ^{51}V nucleus ($I = 7/2$), and with $g_{\parallel} = 1.932$, $g_{\perp} = 1.980$, $|A_{\parallel}| = 205$ gauss, and $|A_{\perp}| = 75$ G. These values agree with those for usual vanadyl complexes with axial symmetry of ligand field. The g values of isotropic spectra for amorphous catalysts are almost equal to the mean g value for No. 9 ($g_{\parallel} + 2g_{\perp} = 1.964$). Therefore isotropic spectra for amorphous samples are also supposed to be due to usual vanadyl complexes, i.e., vanadyl phosphates in this case.

Maximum slope line widths (ΔH_{msl}) for

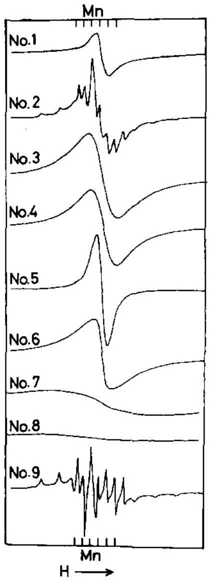

FIG. 2. ESR spectra for various OA-VP samples.

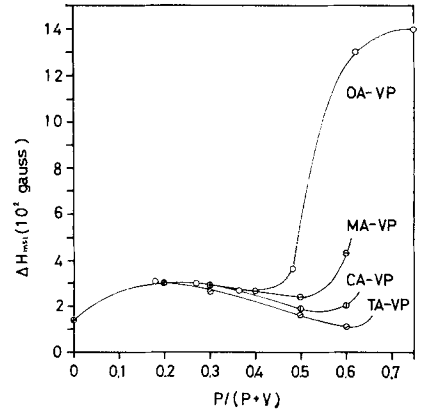

FIG. 3. The relation between phosphor fraction and ΔH_{msl} of ESR spectra for VP catalysts.

these spectra vary with f_p as shown in Fig. 3. The change of line width is closely related to the oxidation number of vanadium ions in these catalysts. The relation between average oxidation number of vanadium ions and ΔH_{msl} of these catalysts is shown in Fig. 4. It is seen from Fig. 4 that ΔH_{msl} increases gradually as the oxidation number decreases from 5.0, and with further decrease of the oxidation number ΔH_{msl} decreases again to come to minimum point at which the oxidation number of vanadium ions is 4.0. In addition it should be noted that ΔH_{msl} increases drastically as the oxidation number decreases from 4.0. For example, as the oxidation number decreases from 4.01 (No. 5) to 3.78 (No. 7) the apparent line width increases from 270 to 1300 G. This fact indicates that small concentration of V^{3+} ions cause the drastic broadening of line width.

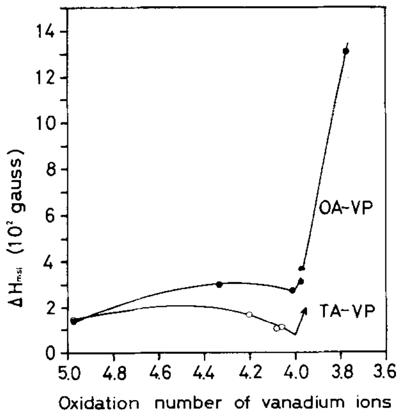

FIG. 4. The relation between the oxidation number of vanadium ions and ΔH_{msl} of ESR spectra for OA-VP and TA-VP.

2. *Structural Change of VP Catalysts by Reduction and Reoxidation*

When OA-VP's were evacuated to about 10^{-3} mm Hg at 250, 300, 350, and 400°C and reoxidized in air at 400°C, apparent line widths of their ESR spectra change as shown in Fig. 5. Each of these treatments was carried out for 5 min. Line widths for VP catalysts with low f_p (Nos. 1–4) change only slightly throughout these treatments. In contrast, the line widths for amorphous catalysts with f_p from 0.36 to 0.75 (Nos. 5–8) change markedly by these treatments: the line widths increase by evacuation and almost reversely decrease by reoxidation. In these experiments, evacuated samples were handled in air during the determination of average oxidation number and ESR and ir measurements, since reoxidation of catalysts hardly occurs in air at room temperature.

Since the change of line width is especially remarkable for No. 6, the change of structures of this sample was studied in more detail. The change of ir and ESR spectra caused by evacuation and reoxida-

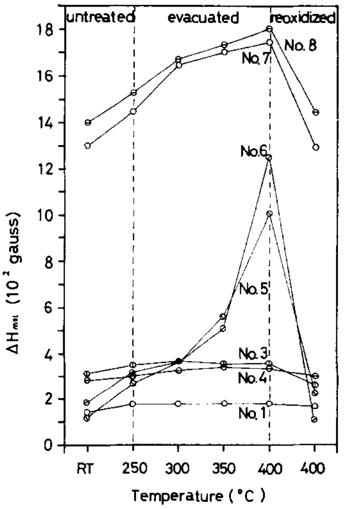

FIG. 5. The change of ΔH_{msl} for OA-VP caused by evacuation and reoxidation.

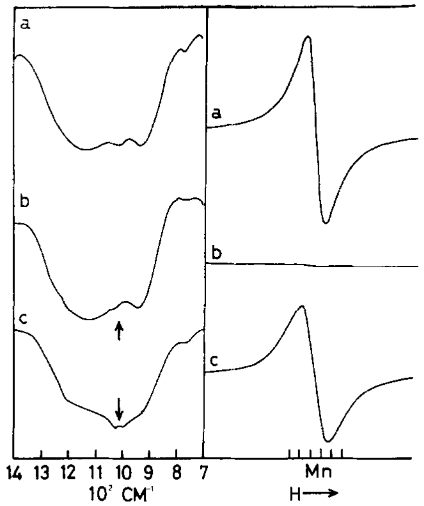

FIG. 6. Infrared and ESR spectra for untreated (a), evacuated (b), and reoxidized (c) sample of No. 6.

tion at 500°C for 1 hr is shown in Fig. 6. By evacuation, the ir band due to V=O stretching vibration at 1010 cm^{-1} is diminished and ESR spectrum becomes so broad that apparently no signal can be observed. In addition, the average oxidation number of vanadium ions decreased from 3.97 to 3.52, and the magnetic susceptibility increased from 8.1×10^{-6} to 11.7×10^{-6}. By reoxidation, the V=O stretching vibration band and the ESR spectrum recovered. These facts indicate that V=O bonds in the amorphous catalysts can be easily broken by evacuation and reformed by reoxidation. Decrease of the oxidation number of vanadium ions from 3.97 to 3.52 indicates that about half of vanadium ions were reduced from V^{4+} to V^{3+} by this treatment.

The broadening of ESR spectra caused by evacuation is supposed to be due to the formation of V^{3+} ions which has a strong effect to broaden the ESR spectrum, as mentioned above. The oxidation number of vanadium ions in sample No. 3 is almost equal to that for No. 6. Nevertheless, vanadium ions in the former are hardly reduced by the evacuation at 500°C. This indicates that reduction and oxidation of amorphous VP catalysts occur more easily than crystalline catalysts.

3. The Influence of Reducing Agent of NH_4VO_3 on the Structures of VP Catalysts

In the course of this study, it was found that α-hydroxy carboxylic acid (HCA) such as malic acid, tartaric acid, and citric acid can also reduce ammonium metavanadate. VP catalysts obtained by using these reagents are also amorphous and supposed to be vanadyl phosphates in the region of high $f_p (\geq 0.4)$. However they are different from OA-VP in their detailed structures.

Infrared spectra for OA-VP and TA-VP with the same component ($f_p = 0.6$) are shown in Fig. 7. It is seen that the peak of the absorption band corresponding to P–O stretching vibration is shifted from 1120 cm^{-1} for OA-VP to about 1200 cm^{-1} for TA-VP. Since P–O stretching vibration bands are known to shift to high wave number region as the degree of condensation of phosphoric ion becomes large (*5*), this fact indicates that the degree of condensation of phosphoric ion in TA-VP is larger than that in OA-VP. MA-VP and CA-VP give ir spectra similar to those for TA-VP.

The structural difference between OA-VP and HCA-VP can also be detected by ESR. The relation between ΔH_{msl} of ESR spectra and f_p for OA-VP and HCA-VP is shown

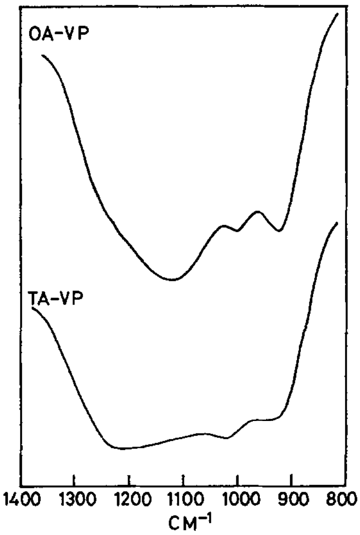

FIG. 7. Infrared spectra for OA-VP and TA-VP with f_p of 0.6.

in Fig. 3. Line widths of ESR spectra for VP catalysts with f_p smaller than 0.2 are not affected by the kind of used reducing agent. On the contrary, line widths for VP catalysts with f_p larger than 0.3 depend on the kind of reducing agent. Especially, in the region of f_p larger than 0.5, the difference of ΔH_{msl} is remarkable. This suggests that microscopic structures of VP catalysts with high f_p depends on the kind of reducing agent of ammonium metavanadate.

4. Catalytic Activity of VP Catalysts

VP catalysts with low f_p are usually so active that total oxidation of butene-1 occurs, resulting in the low selectivity of maleic anhydride. At the reaction temperature of 400–500°C, VP catalysts with $f_p = 0.5$–0.7 give high yield of maleic anhydride. The results of butene-1 oxidation are shown in Tables 2 and 3. The space velocity of reactant gas which contains 99.5 vol% of air and 0.5 vol% of butene-1, was 5700 cc/(cc catalyst·hr).

The relation between f_p and the conversion of butene-1 and the yield of maleic anhydride at the reaction temperature of 450°C is shown in Fig. 8. As shown in Fig. 8, the conversion of butene-1 decreases, as f_p increases from 0.5 to 0.65 for OA-VP. However MA-VP, TA-VP, and CA-VP are active at higher f_p region, and the conversion of butene-1 is almost 100% even at $f_p = 0.65$. As f_p increases from 0.65, the conversion of butene-1 decreases rapidly for MA-VP and TA-VP. CA-VP is active even at $f_p = 0.68$. The yield of maleic anhydride for OA-VP is maximum at $f_p = 0.55$. On the other hand, TA-VP and CA-VP give maximum yield at $f_p = 0.65$–0.68, and maximum yield for these catalysts (60–65 mol%) is considerably larger compared to that for CA-VP (below 50 mol%).

The oxidation numbers of vanadium ions in VP catalysts after reaction vary with f_p as shown in Fig. 9. The oxidation numbers decrease from about 4.7 to about 3.8, as f_p increases from 0.5 to 0.7.

The relation between the oxidation numbers of vanadium ions in VP catalysts after the reaction and the yield of maleic anhydride and the conversion of butene-1 is shown in Fig. 10. As seen from Fig. 10, in the range where the conversion of bu-

TABLE 2

RESULTS OF BUTENE-1 OXIDATION BY OA-VP AND MA-VP

		OA-VP			MA-VP		
	Reaction temp	Conv.	Yield (mol%)		Conv.	Yield (mol%)	
f_p	(°C)	(%)	MAn	HOAc	(%)	MAn	HOAc
0.50	400	89.1	27.0	9.6	95.2	33.0	12.1
	450	96.8	23.7	3.5	99.5	32.9	5.1
	500	95.1	14.1	1.1	99.5	23.7	0.8
0.55	400	77.3	32.2	7.0	99.4	46.1	6.8
	450	91.2	36.7	4.6	99.9	42.2	1.6
	500	98.0	33.9	1.8	99.7	27.7	0.6
0.60	400	54.6	19.9	4.8	86.4	38.5	8.0
	450	76.4	33.4	3.9	99.6	51.0	4.5
	500	93.6	38.0	2.6	99.9	42.4	0.7
0.65	400	28.4	2.7	0.5	30.6	10.4	1.7
	450	41.7	11.0	1.0	77.8	35.2	3.3
	500	70.8	25.9	1.9	97.8	45.2	2.0
0.70	400				14.2	0.0	0.0
	450				12.5	0.0	0.0
	500				22.5	2.4	0.9

TABLE 3
RESULTS OF BUTENE-1 OXIDATION BY TA-VP AND CA-VP

		TA-VP			CA-VP		
	Reaction temp		Yield (mol%)			Yield (mol%)	
f_p	(°C)	Conv. (%)	MAn	HOAc	Conv. (%)	MAn	HOAc
0.50	400	99.9	14.4	4.0	97.9	26.3	6.2
	450	99.8	10.1	0.7	98.8	19.5	1.2
	500	99.0	8.3	0.0	92.2	5.4	0.0
0.55	400	98.4	35.5	8.1	99.0	40.9	6.6
	450	99.8	35.4	1.3	99.9	39.0	1.3
	500	99.4	16.3	0.9	99.6	30.1	0.0
0.60	400	96.1	43.4	7.2			
	450	99.8	50.0	3.4			
	500	99.9	44.4	1.0			
0.65	400	53.5	21.3	4.2	94.1	47.6	8.3
	450	97.9	62.4	4.5	99.8	52.7	2.1
	500	99.9	61.0	2.1	99.9	52.5	0.3
0.68	400				59.4	26.0	4.8
	450				99.7	62.8	2.7
	500				99.9	57.1	0.0
0.70	400	13.5	2.5	0.3	42.2	11.1	2.3
	450	21.2	7.5	0.6	75.8	36.6	2.1
	500	62.4	22.3	0.7	99.1	49.2	1.5

tene-1 is almost 100%, the yield of maleic anhydride increases linearly as the oxidation number decreases. For TA-VP and CA-VP maximum yield of maleic anhydride is obtained when the oxidation number is 4.0, and the conversion and the yield decrease rapidly as the oxidation number becomes smaller than 4.0. This result indicates that the activity and the selectivity of VP catalysts strongly depend upon the oxidation number of vanadium ions.

The oxidation number of vanadium ions can be controlled not only by changing the composition of the catalyst, but also by changing the reaction condition such as space velocity of reactant gas. Figure 11

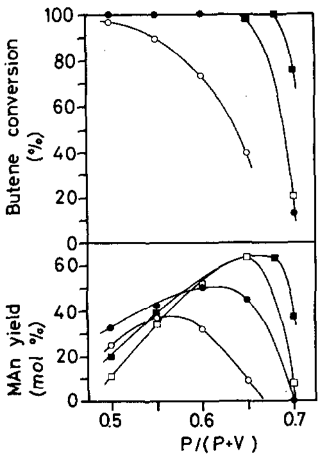

FIG. 8. The results of butene-1 oxidation. (○) OA-VP, (●) MA-VP, (□) TA-VP, (■) CA-VP.

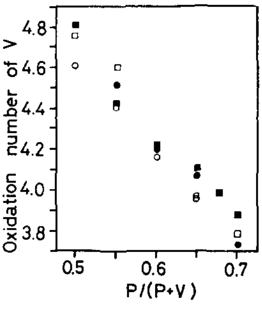

FIG. 9. The oxidation number of vanadium ions in VP catalysts after the reaction. Symbols are same as in Fig. 8.

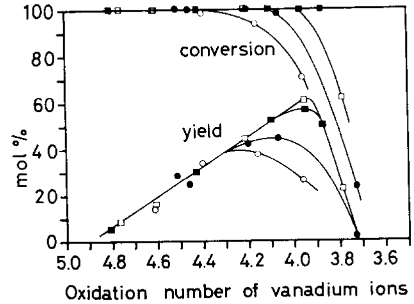

FIG. 10. The relation between the oxidation number of vanadium ions in reacted VP catalysts and the conversion of butene-1 and the yield of maleic anhydride. Symbols are same as in Fig. 8.

shows the dependency of the conversion of butene-1, the yield of maleic anhydride and acetic acid, and the oxidation number of vanadium ions in reacted VP catalysts at entrance and exit parts of reaction tube, upon the space velocity of reactant gas. The catalyst used was CA-VP with f_p = 0.65. Reaction was carried out at 450°C with the concentration of butene-1 fixed to 0.5 vol%. At low SV, the oxidation number of vanadium ions at entrance part is smaller than 4.0, whereas that at exit part is larger than 4.0. As SV increases, the oxidation numbers at both parts approach to each other, and become almost equal to 4.0 at SV = 5000, and at this SV the yield of maleic anhydride becomes maximum. As SV increases furthermore, the oxidation numbers at both parts become smaller than 4.0, and the yield of maleic anhydride decreases.

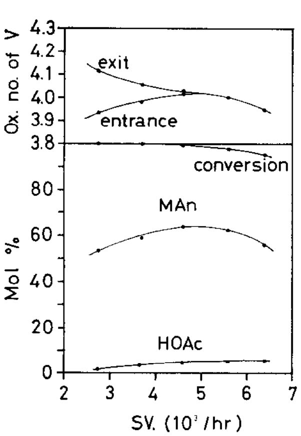

FIG. 11. The effect of SV of reactant gas upon the results of butene-1 oxidation and upon the oxidation number of vanadium ions in reacted VP catalysts placed at entrance and exit parts of reaction tube.

Thus, in the case of TA-VP and CA-VP, the yield of maleic anhydride becomes maximum when the oxidation number of vanadium ions is 4.0, regardless of whether the oxidation number is controlled by changing the component of the catalyst or by changing the SV of reactant gas.

DISCUSSION

1. *Line Widths of ESR Spectra for Amorphous VP Catalysts*

Line shapes of isotropic ESR spectra for amorphous VP catalysts are very close to Lorentzian ones. This suggests the existence of the electronic exchange interactions between vanadium ions (*6*). Two types of exchange interactions must be considered in this case. One is between V^{4+} ions, and another is between V^{3+} and V^{4+} ions. The former results in so-called exchange narrowing. On the other hand, the latter is supposed to cause line broadening, because V^{3+} ions with high spin d^2 configuration have a very short spin-lattice relaxation time. ESR spectra for V^{3+} ions are generally so broad that it can be observed only at low temperature such as liquid helium temperature (*7*). Therefore, if the exchange interaction exists between V^{4+} ions and V^{3+} ions, ESR spectrum of V^{4+} ions will be broadened by only a small quantity of V^{3+} ions.

As mentioned above (Figs. 3 and 4), line width for amorphous VP catalysts becomes minimum when the oxidation number of vanadium ions is 4.0. This narrowing of ESR spectra is supposed to be due to the electronic exchange interaction between V^{4+} ions. On the other hand, rapid increase of line width accompanied by the decrease of the oxidation number of vanadium ions below 4.0 is supposed to be due to the exchange interaction between V^{3+} and V^{4+} ions.

The oxidation number of vanadium ions in the VP catalyst No. 9 is 3.17. Nevertheless, this catalyst gives a spectrum with well-resolved ^{51}V hyperfine structure. This suggests that V^{4+} and V^{3+} ions in this catalyst are electronically isolated by excess of phosphoric ions.

2. *Structural Difference Between OA-VP and HCA-VP*

As shown in Fig. 3, HCA-VP's give ESR spectra with narrower line width than OA-VP's at high f_p region. Especially, TA-VP and CA-VP with f_p from 0.5 to 0.6 give very sharp ESR spectra. For example, the line width for TA-VP with $f_p = 0.6$ is 110 G. This value is the smallest one as the apparent line width of ESR spectrum for the powder sample of the compound of V^{4+} ion, as far as we know. The exchange narrowing of ESR spectrum has been observed for V^{4+} ions in single crystals of vanadium pentoxide prepared by zone melting method (*8*). In this case, exchange interaction between adjacent two and next neighboring eight V^{4+} ions has been proved by observing the hyperfine structures due to two and eight vanadium nuclei, respectively. However even in this case, ΔH_{msl} for the powder sample was 130 G at room temperature. These facts lead us to conclude that vanadium ions in TA-VP and CA-VP occur in microscopically dense clusters in which several V^{4+} ions are connected by electronic exchange interaction. On the other hand, vanadium ions in OA-VP are supposed to be rather homogeneously dispersed. The degree of aggregation of vanadium ions in MA-VP is supposed to be intermediate of OA-VP and TA-VP.

3. *The Relation Between the Structure and the Catalytic Activity*

Results of butene-1 oxidation show that the activity and the selectivity of VP catalysts with high f_p increase in the order of OA-VP < MA-VP < TA-VP, CA-VP. This order agrees with the order of the degree of aggregation of vanadium ions. This indicates that the activity and the selectivity of VP catalysts increase as the aggregation of vanadium ions becomes remarkable.

As shown in Fig. 10, the yield of maleic anhydride is maximum, when the oxidation number of vanadium ions in reacted catalysts is 4.0, and the yield decreases rapidly as the oxidation number becomes smaller than 4.0. This indicates that in the absence of V^{5+} ions maleic anhydride is hardly produced, and this in turn suggests that the redox cycle between V^{5+} and V^{4+} ions is mainly concerned with the reactions from butene-1 to maleic anhydride.

Recently, oxygen species such as O_2^- and O^- have been detected on a variety of metal oxides (*9*). However these adsorbed oxygen species are not supposed to be active centers for the formation of maleic anhydride, since these species can be found not only on the oxides of vanadium and molybdenum, but also on the metal oxides inactive for the synthesis of maleic anhydride such as titanium oxide and zinc oxide (*10*).

Oxides of vanadium and molybdenum as well as phosphates of these metal ions catalyze the formation of maleic anhydride from butene, and it was found in our laboratory that all of these catalysts contain metal–oxygen double bond as detected by ir spectroscopy in the region of 950–1050 cm^{-1}. In addition, important roles of metal–oxygen double bonds in catalytic activities have been pointed out by several workers (*1*, *11*). Therefore it seems most likely that the V=O bond is the active center for the formation of maleic anhydride.

In order to reduce an oxygen molecule in air into two of O^{2-} ions of V=O bonds, four electrons are necessary. These electrons are supposed to be supplied from four V^{4+} ions.

$$O_2 + 4V^{4+} \rightarrow 2O^{2-} + 4V^{5+}.$$

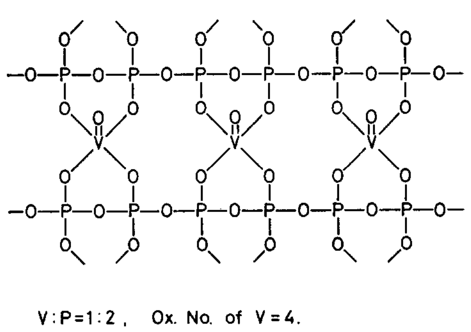

FIG. 12. Schematic representation of the vanadyl phosphate with V:P = 1:2 and oxidation number of all vanadium ions is 4.0.

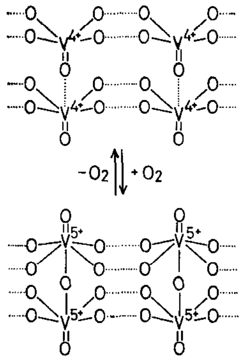

FIG. 13. A model for active centers in the VP catalysts. Horizontal dotted lines correspond to phosphate ions.

In vanadyl phosphate catalysts, V^{4+} ions exist as V$=$O^{2+} ions, as proved by their ESR and ir spectra. Figure 12 is a schematic representation of a vanadyl phosphate in which all vanadium ions exist as V$=$O^{2+}, and the atomic ratio of V:P is 1:2. CA-VP and TA-VP with this atomic ratio give maximum yield of maleic anhydride (Fig. 8).

In Fig. 13, a schematic representation of the active center in vanadyl phosphate catalysts is shown. In Fig. 13, horizontal dotted lines correspond to phosphoric ions. In this model it is assumed that electrons can move through vertical V$=$O . . . V bonds of reduced state and V–O–V bonds of oxidized state. Remarkable exchange narrowing observed for TA-VP and CA-VP is also supposed to be caused by the electronic exchange interaction between V^{4+} ions through these bonds.

ACKNOWLEDGMENT

The authors are indebted to Professor S. Fujiwara (Faculty of Science, Tokyo University) for helpful discussions. The authors also express thanks to Dr. H. Tadano (Faculty of Science, Rikkyo University) for providing the apparatus for measurement of magnetic susceptibility.

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