

Preparation of Vanadium-Phosphorus Mixed Oxide (P/V=1) Catalysts and Their Application to Oxidation of Butane to Maleic Anhydride

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Several vanadium-phosphorus mixed oxides with a P/V ratio=1 have been prepared and the relationships between the structure of catalyst and the catalytic function for the selective oxidation of butane to maleic anhydride were examined. As revealed from XRD, IR, XPS, and redox titration studies, five among them were presumably composed of crystalline single phases, that is, α -VOPO₄, β -VOPO₄, and (VO)₂P₂O₇ as well as unknown phases X₁ and X₂. The valences of the vanadium of these catalysts were close to five, except for (VO)₂P₂O₇ (the valence was four). These phases were prepared, respectively, by controlling the kind of precursors and the calcination conditions. The selectivity to maleic anhydride differed markedly among these catalysts, although the rate did not change much when it was normalized to surface area. The selectivity at 440 °C was less than 20% for α - and β -VOPO₄, 40% for X₁ and X₂, and 70% for (VO)₂P₂O₇. Amorphous phases having V⁴⁺ were much less selective than (VO)₂P₂O₇. No structural changes of the catalysts after use were observed in the cases of α -, β -VOPO₄, and (VO)₂P₂O₇. Therefore, the effective phase for selective oxidation of butane to maleic anhydride was speculated to be a phase like (VO)₂P₂O₇ in which the valence of vanadium is four and the structure is stable under the reaction conditions.

Vanadium-phosphorus mixed oxides are known as catalysts for the selective oxidation of butene to maleic anhydride.¹⁾ Several basic studies have been reported on the active structure of the catalysts,²⁾ the role of phosphorus,^{2–4)} and the reaction mechanism.³⁾ The preferred atomic ratio of phosphorus to vanadium is usually in the range of 1.2 to 2.0.

Recently, certain V-P oxides with a P/V ratio of between 1.0 and 1.2 were found to be efficient catalysts for the selective oxidation of butane, a saturated hydrocarbon, to maleic anhydride.^{1,5)} Several studies on V-P oxide catalysts in this composition range have also been reported.^{6–10)} However, in most studies, the V-P oxide catalysts used had various P/V ratios, and they usually contained unknown phases or were mixtures. Therefore, the real active phase for the butane oxidation still remains unclarified, although there are many proposals in patents for the preparation of effective catalysts.^{11–14)}

It was recently indicated that nearly crystalline phases with P/V ratios close to unity were active and selective for the oxidation of butane.^{6,7,10,14)} As for V-P oxide with P/V=1, crystalline phases such as α -VOPO₄, β -VOPO₄, and (VO)₂P₂O₇ are known.^{15–18)} These facts motivated us to study these catalysts in greater detail as an extension of our studies on oxidation catalysts having well-defined bulk structures.

In the present study we attempted (i) to examine more extensively the preparation process of catalysts having single crystalline phases with P/V=1, by using well-defined precursors and (ii) to specify the phase or structure of a catalyst which is efficient for the oxidation of butane. An elucidation of the mechanism of catalytic action and the reason why that phase is effective will be the subjects of following study.

Experimental

1. Catalyst Preparation. **1.1. Precursors:** Three kinds of V-P-O compounds (P/V=1) with well-defined structures (denoted as P-I, -II, and -III) have been prepared as precursors for catalysts.

(a) (NH₄)₂[(VO)₂C₂O₄(HPO₄)₂]·5H₂O (P-I). P-I was prepared according to the literature.¹⁹⁾ V₂O₅ powder (0.1 mol) was added gradually with stirring into 400 ml of an aqueous solution of oxalic acid (0.75 mol l⁻¹) at 80 °C. When the solution turned to blue after a few minutes, NH₄H₂PO₄ (0.2 mol) was added. A green precipitate was formed while the stirring continued. The precipitate was filtrated, washed with water and acetone, and dried overnight at 100 °C. The obtained solid was confirmed to be (NH₄)₂[(VO)₂C₂O₄(HPO₄)₂]·5H₂O by comparing X-ray diffraction powder patterns (XRD) with a reference.¹⁹⁾

(b) NH₄HVPO₆ (P-II). This precursor (P-II) was prepared according to the literature.¹⁵⁾ V₂O₅ powder (0.04 mol) was added to a boiling aqueous solution of NH₄H₂PO₄ (0.8 mol in 600 ml H₂O), and boiling was maintained for 30 min. A yellow precipitate was formed after the solution was allowed to stand overnight. The precipitate was filtrated, washed with water and acetone, and dried overnight at 100 °C. The XRD pattern (d/Å: 8.75 (100), 4.60 (2), 4.46 (3.5), 4.41 (3), 4.09 (3), 3.17 (3), 2.95 (15), relative peak intensity in parentheses) indicated that P-II was well crystallized. However, an identification was not made because of the absence of reference data.

(c) (VO)₂H₄P₂O₉²⁰⁾ (P-III-1, 2, and 3). P-III-1 was prepared according to the literature.^{14a)} V₂O₅ powder (0.1 mol) was added to an aqueous solution (200 ml) of NH₂OH·HCl (0.2 mol, Nakarai Chemicals) and H₃PO₄ (0.2 mol, Koso Chemicals) at 80 °C and was stirred for 1 h, in order to completely reduce V₂O₅. After the solution became a light-blue slurry of about 100 ml, it was evaporated to dryness at 130 °C overnight. A small quantity of water (100 ml) was added to the dried solid and the mixture was boiled for 10 min. A light green precipitate obtained by filtration was washed with water. The structure was confirmed by its XRD pattern with reference to the literature.²⁰⁾

P-III-2 was prepared in a similar manner as P-III-I. The

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TABLE 1. STARTING MATERIALS OF PRECURSORS

Precursor	Starting Materials
P-I	$(\text{NH}_4)_2[(\text{VO})_2\text{C}_2\text{O}_4(\text{HPO}_4)_2]$ V_2O_5 , $(\text{COOH})_2$, $\text{NH}_4\text{H}_2\text{PO}_4$
P-II	NH_4HVPO_6 V_2O_5 , $\text{NH}_4\text{H}_2\text{PO}_4$
P-III-1	$(\text{VO})_2\text{H}_4\text{P}_2\text{O}_9$ V_2O_5 , $\text{NH}_2\text{OH} \cdot \text{HCl}$, H_3PO_4
P-III-2	$(\text{VO})_2\text{H}_4\text{P}_2\text{O}_9$ V_2O_5 , $\text{NH}_2\text{OH} \cdot \text{HCl}$, H_3PO_4 , $\text{C}_3\text{H}_4\text{O}_3$
P-III-3	$(\text{VO})_2\text{H}_4\text{P}_2\text{O}_9$ V_2O_4 , H_3PO_4

only difference was that ethylene carbonate ($\text{C}_3\text{H}_4\text{O}_3$, Nakarai Chemicals) was added to the solution before concentration in order to eliminate Cl.^{14b)} The XRD pattern was very similar to that of P-III-1; however, the peaks were weaker.

P-III-3 was prepared using V_2O_4 . A V_2O_4 powder (0.05 mol, Aldrich) was dissolved into an aqueous solution of H_3PO_4 (0.1 mol in 100 ml H_2O) at 80°C. The resultant blue solution was concentrated at 80°C with stirring into a green paste. After the green paste was dried at 100°C, it was placed into water. A light-blue precipitate was obtained upon filtration and washing with water.

Table 1 summarizes the composition and starting materials of the precursors.

1.2 Calcination of Precursors. The precursors were calcined (a) in streams of O_2 or N_2 in a reactor or (b) in air by use of a muffle furnace.

(a) Each precursor (2–5 g) was calcined in Pyrex-tube reactors (10 or 20 mm in diameter) under the flow of oxygen or nitrogen at a prescribed temperature. The heating rate was controlled by adjusting the power, and the temperature was continuously monitored. The flow rate was 100–200 ml min^{-1} . To avoid any blockage of gas flow due to melting, the heating rate was kept low and a wide reactor diameter was adopted.

(b) In the case of any calcination in air, a muffle furnace was used. The heating rate was about 30°C min^{-1} .

2. Characterization of Catalysts. **2.1 XRD and IR:** XRD powder patterns of precursors and catalysts were recorded using a Rigaku X-ray diffractometer with $\text{Cu K}\alpha$ radiation filtered by Ni. The XRD was also measured for the catalysts after use. Infrared spectra were recorded with a spectrometer (JIR-10, FT-IR) using an KBr supporting disc.

2.2 XPS: XPS measurements of fresh and used catalysts were carried out using an ESCA Lab 5 (Vacuum Generator). The excitation was performed with the $\text{Mg K}\alpha$ line. Binding energies were referred to the C_{1s} line (285 eV). Samples were evacuated under 10^{-8} Torr (1 Torr = 133.3 Pa) at 25°C in the ESCA chamber.

2.3 Valence of Vanadium: The average oxidation state of vanadium in the catalysts was determined by redox titration.⁹⁾ About 0.1 g of each catalyst was dissolved in 100 ml of 2 M[†] H_2SO_4 at 80°C. The vanadium (IV or III) content was determined by titration with a solution of KMnO_4 (0.1 M). The vanadium (V) content was determined by titration with a solution of a Mohr salt ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, 0.1 M) using diphenylamine as an indicator.

2.4 Surface Area: The surface areas of the catalyst were measured by the BET method (N_2 adsorption).

3. Measurement of Catalytic Activity and Selectivity. The oxidation of butane was carried out using a conventional fixed-bed flow reactor at atmospheric pressure. The reactor was a Pyrex tube (10 mm in diameter) and was externally

heated by an electric furnace. The feed gas consisted of 1.5 vol% butane, 17 vol% oxygen and nitrogen (balance). The reaction temperature was from 250°C to 440°C. Products containing carbon were maleic anhydride (MA), CO and CO_2 . No other products (C_2 – C_3 aldehydes and carboxylic acids) were detected (less than 1%). The carbon balance at the stationary state was always almost 95–100%. Maleic anhydride was collected by a cold trap and was determined by titration with 0.1 M NaOH .⁶⁾ Gaseous products were analyzed by a gas chromatograph. It was confirmed, in some cases, that no products other than MA were trapped.

Results

1. Effects of Calcination Conditions on the Structure of V–P Oxide Catalysts.

1.1 Calcination in O_2 or Air: The structures of the catalysts obtained by calcination in an O_2 or air flow are summarized in Table 2. The results show that the kinds of precursors, the calcination temperature and the heating rate, all, greatly affect the structure of formed catalysts. For example, a high heating rate caused the formation of β - VOPO_4 from P-I, while α - VOPO_4 was formed from the same precursor using a low heating rate. At an intermediate heating rate, a mixture of α - and β -phase was obtained.

When P-II was calcined at 550 and 600°C at a low heating rate, a new XRD pattern ($d/\text{\AA}$: 4.72 (40), 4.11 (100), 3.15 (30), relative intensity in parentheses) different from either α -, β - VOPO_4 or $(\text{VO})_2\text{P}_2\text{O}_7$ was observed. A high S/N ratio of the XRD peaks, together with the fact that the same XRD patterns were obtained for two samples containing this phase; indicates that this was a single phase. This will be denoted as X_1 in this paper.

The influence of the calcination temperature is seen from the results obtained at a heating rate of 30°C min^{-1} . The calcination of P-I at 450°C formed almost an amorphous phase (weak peaks at $d/\text{\AA}$: 4.33, 4.17, 3.91, 3.65, 3.50, and 3.10), while after a calcination at 550 or 600°C, the resultant catalysts were crystalline. This showed that XRD patterns are ascribable to pure β - VOPO_4 . Changes in the phase with the calcination temperature was also found in the case of P-II. A new phase denoted by X_2 ($d/\text{\AA}$: 4.00 (90), 3.66 (45), 3.12 (100), relative intensity in parentheses), was obtained by a low-temperature calcination. X_1 and X_2 were water-soluble and the solution was acidic (pH was 2.37 at about 2 g l^{-1} for X_1 and X_2), while α -, β - VOPO_4 , and $(\text{VO})_2\text{P}_2\text{O}_7$ were water-insoluble.

The calcination of P-III-1, 2, containing vanadi-

[†] 1 M = 1 mol dm^{-3} .

TABLE 2. STRUCTURES OF CATALYSTS OBTAINED BY CALCINATION IN O₂ OR AIR

Precursor	in	Rate/°C min ⁻¹	T/°C	Time/h	Phase formed ^{a)}	Cat. No. ^{b)}
P-I	O ₂	2.9	600	10	α -VOPO ₄	1
	O ₂	5.0	600	10	α + β	
	O ₂	6.4	550	10	β -VOPO ₄	2
	O ₂	7.0	600	10	β -VOPO ₄	
	Air	30	450	20	Unknown	3
P-II	Air	30	550	16	β -VOPO ₄	
	Air	30	450	20	X ₂	6
	Air	30	500	20	X ₁ + β	
	O ₂	3.3	550	10	X ₁	5
	O ₂	3.3	600	10	X ₁	
P-III-1	O ₂	7.5	550	10	β +X ₁	4
	Air	30	600	16	β -VOPO ₄	
	Air	30	450	20	(VO) ₂ P ₂ O ₇ +X ₁	4
	Air	30	600	20	β +(VO) ₂ P ₂ O ₇ +X ₁	
	O ₂	3.0	600	10	Unknown+X ₁ +X ₂ + α	4
P-III-2	Air	30	450	20	X ₁ +(VO) ₂ P ₂ O ₇	
	Air	30	600	20	X ₁ + β	

a) In the case of mixtures, the main phases are given in the first place. b) The catalyst numbers are the same as those in Tables 4 and 5.

TABLE 3. STRUCTURES OF CATALYSTS OBTAINED BY CALCINATION IN N₂^{a)}

Precursor	Time/h	Phase formed	Cat. No. ^{b)}
P-I	10	Amorphous	7
P-II	6	Amorphous	8
P-III-1	2	(VO) ₂ P ₂ O ₇	9
P-III-2	2	Unknown	
P-III-3	2	(VO) ₂ P ₂ O ₇	

a) 550°C. heating rate; 10°C min⁻¹. b) The catalyst numbers are the same as those in Tables 4 and 5.

um(IV) in air or O₂ yielded mixed phases. The content of (VO)₂P₂O₇ tended to increase as the calcination temperature decreased or the heating rate increased.

1.2 Calcination in N₂: Table 3 shows the results for the calcination at 550°C in N₂ with a heating rate of 10°C min⁻¹. P-I and P-II were converted to amorphous phases, while P-III-1 and P-III-3 readily changed to (VO)₂P₂O₇. Less crystalline P-III-2 gave a phase with weak XRD peaks which are not ascribable to (VO)₂P₂O₇.

(VO)₂P₂O₇ (obtained by the calcination of P-III-1 in N₂) was insoluble in water. However, when it was heated in O₂ (500°C, 2h), a part of the solid became soluble in the water and the solution became brown. Figure 1 shows the changes of XRD patterns of P-III-1 and P-III-2 due to these processes. After heating P-III-1 in N₂, a typical XRD pattern due to (VO)₂P₂O₇ was found (Fig. 1A). The subsequent treatment with O₂ at 500°C caused a partial formation of X₁. By washing with water, the intensity of the XRD peaks due to (VO)₂P₂O₇ increased by a factor of about 2; no peaks other than (VO)₂P₂O₇ appeared. The changes in the XRD peaks during this procedure were clearer in the case of P-III-2, as shown in Fig. 1B. The weight loss observed by washing with water was about 50% for the latter case.

2. Characterization of Catalyst.

The surface area

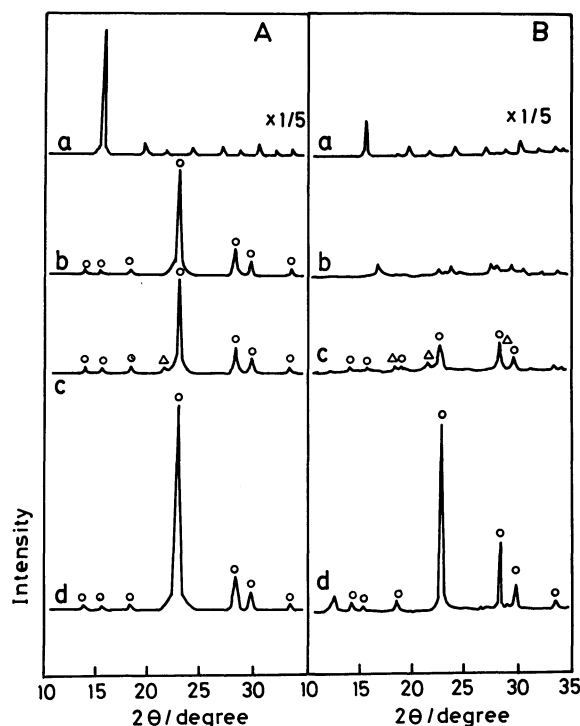


Fig. 1. Changes of XRD patterns by calcination and washing water.

A: P-III-1, B: P-III-2. ○; (VO)₂P₂O₇, Δ; X₁.

a) Precursors, b) After calcination at 550°C in N₂, c) After calcination at 550°C in O₂, d) After washing with H₂O.

of catalysts and the valence state of vanadium are summarized in Table 4. The surface area decreased as follows: X₁, X₂>(VO)₂P₂O₇> α -VOPO₄>Amorphous $\geq$ β -VOPO₄. The oxidation states were close to five for α -, β -VOPO₄, X₁, and X₂ and that of (VO)₂P₂O₇ was essentially four. The valence was lower than four after P-I and P-II were heated in N₂ at 550°C.

Typical XRD patterns of these phases are shown

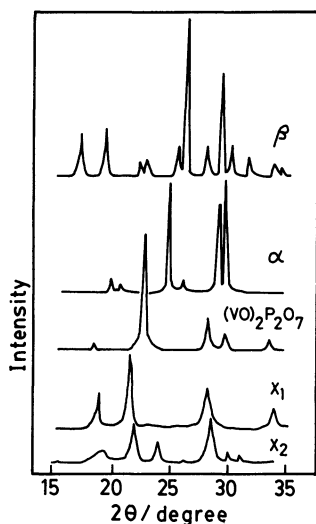


Fig. 2. Typical XRD patterns of V-P oxides prepared.

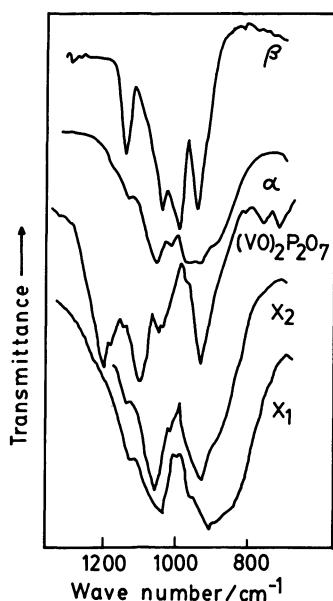


Fig. 3. Infrared spectra of V-P oxides prepared.

in Fig. 2. Figure 3 shows the infrared spectra of the catalysts in the region of 800–1200 cm⁻¹. This region corresponds to the stretching modes of P–O and V=O. The spectra for α -, β -VOPO₄ and (VO)₂P₂O₇ were in agreement with those reported in the literature.^{15,21)} The spectra of X₁ and X₂ (1170, 1080, and 955 cm⁻¹) were similar to each other.

XPS spectra of β -VOPO₄ and (VO)₂P₂O₇ are shown in Fig. 4. The peaks at 526.1 and 519 eV for β -VOPO₄ are assigned to 2p_{1/2} and 2p_{3/2} of vanadium (V) and those at 524.6 and 517.7 eV to 2p_{1/2} and 2p_{2/3} of vanadium (IV).²²⁾ Although the surfaces of metal oxides are sometimes in more oxidized states than in the bulk, e.g., Fe₂O₃ at the surface of Fe₃O₄,²³⁾ the oxidation states of the catalysts prepared in the present study were very close to those in the bulk. Therefore, it is probable that the crystalline bulk structures were

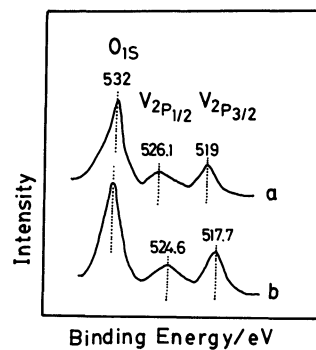
Fig. 4. XPS spectra of β -VOPO₄ and (VO)₂P₂O₇. a): β -VOPO₄, b): (VO)₂P₂O₇.

TABLE 4. SURFACE AREAS AND VALENCE STATES OF VANADIUM OF CATALYSTS

Phase	Surface area/m ² g ⁻¹	Valence of Vanadium	Cat. No.
α -VOPO ₄	5.9	4.97	1
β -VOPO ₄	3.4	—	2
β -VOPO ₄	1.7	4.99	3
β -VOPO ₄	1.3	—	4
X ₁	16.0	4.96	5
X ₂	14.1	4.96	6
Amorphous	3.8	3.34	7
Amorphous	3.5	3.77	8
(VO) ₂ P ₂ O ₇	7.1	4.02	9
(VO) ₂ P ₂ O ₇ ^{a)}	12.4	4.00	10

a) After O₂-treatment at 500°C, washing with H₂O, and recalcination.

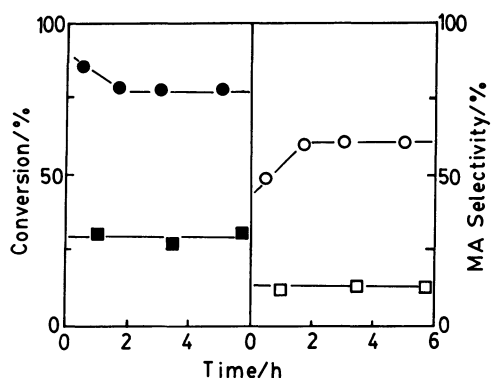


Fig. 5. Activity and selectivity for oxidation of butane at 440°C.

●○; (VO)₂P₂O₇, ■□; β -VOPO₄.

Reaction conditions; butane 1.5%, O₂ 17%, W/F = 0.67 × 10³ g · h · mol⁻¹.

maintained on the surface of these catalysts. The XPS spectra of β -VOPO₄ and (VO)₂P₂O₇ did not change after they were used for the oxidation of butane.

3. Catalytic Oxidation of Butane to Maleic Anhydride (MA).

Catalysts 1 to 10 (catalyst numbers in Tables 2–4) were used for the oxidation of butane. Typical time courses of the reaction over β -VOPO₄ (catalyst 3) and (VO)₂P₂O₇ (catalyst 10) are shown in Fig. 5. β -VOPO₄ showed a constant conversion and selectivity from the beginning of the reaction. α -VOPO₄ (catalyst

TABLE 5. CHANGES OF PHASES AND VALENCE DURING REACTION

Phase	$W/F^a)$	Conv. %	Rate ^{b)}	Selectivity/ C_4 -base%			Phase after reaction ^{c)}	Valence of V ^{d)}	Cat. No.
				CO	CO ₂	MA			
α -VOPO ₄	0.67	53	7.8	57	25	18	α -VOPO ₄	4.99	1
β -VOPO ₄	0.67	62	9.1	61	21	18	β -VOPO ₄	—	2
β -VOPO ₄	0.67	31	4.6	61	25	14	β -VOPO ₄	4.99	3
β -VOPO ₄	0.67	14	2.1	53	27	20	β -VOPO ₄	—	4
X ₁	0.67	59	8.7	44	16	40	α +X ₂	4.97	5
X ₂	0.67	52	7.7	41	15	44	α +X ₂	4.99	6
Amorphous	0.67	61	9.0	69	15	16	α + β	—	7
Amorphous	0.54	15	2.7	51	5	44	X ₂ + α	—	8
(VO) ₂ P ₂ O ₇	0.33	27	7.9	20	8	72	(VO) ₂ P ₂ O ₇	4.05	9
(VO) ₂ P ₂ O ₇ ^{e)}	0.13	35	25.8	23	10	67	(VO) ₂ P ₂ O ₇	4.11	10

a) $10^3 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$. b) $10^{-4} \text{ mol}(\text{g} \cdot \text{h})^{-1}$. c) In the case of mixtures, the main phases are given in the first place. d) After reaction. e) After washing with water (see text).

1) showed a result similar to β -VOPO₄. In the case of (VO)₂P₂O₇, the activity and selectivity changed slightly at first, and became constant after 2 h. For X₁ and X₂, both the activity and selectivity gradually increased for an initial 3 h. Changes were also observed for amorphous catalysts.

The catalytic activity and selectivity for the oxidation of butane at 440°C are summarized in Table 5. Data for the stationary state are given in this table. The (VO)₂P₂O₇ which was washed and recalcined was most active; however, the catalytic activity was more or less similar when normalized to surface area. The activity of β -VOPO₄ was almost proportional to the surface area of the catalysts. In contrast, the selectivity to MA greatly depended on the structure of the catalyst. It was especially high for (VO)₂P₂O₇ (about 70%). X₁ and X₂ showed moderate selectivity (40%), and the selectivity was low for α - and β -VOPO₄ (20%).

Phase and valence changes of vanadium during the reaction were determined as summarized in Table 5. The XRD patterns changed little after the reaction in the cases of α -, β -VOPO₄ and (VO)₂P₂O₇. However, X₁ and X₂ changed into mixtures of α -VOPO₄ and X₂, for which the compositions were similar. Amorphous phases, catalysts 7 and 8, also changed to mixed phases. The oxidation states of vanadium remained unchanged for α -, β -VOPO₄, X₁, X₂ and (VO)₂P₂O₇, but those for amorphous phases increased to about five.

Figure 6 shows the effects of W/F on the conversion and the selectivity to MA obtained for (VO)₂P₂O₇ and β -VOPO₄, where W is the weight of catalyst and F is the flow rate of butane. The selectivity was nearly constant in this range of conversion, although a slight decrease was observed at a low conversion level for (VO)₂P₂O₇.

The effects of the reaction temperature on the reaction rate and selectivity are shown in Fig. 7 for (VO)₂P₂O₇. The conversion was adjusted to about 40% in order to compare the selectivity, except for the reaction at 250°C. The rate at 250°C was so low that a higher conversion was not attained. The selectivity increased as the reaction temperature decreased and was about

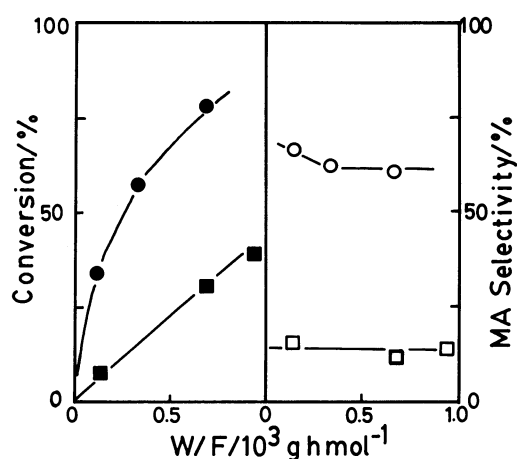


Fig. 6. Effect of W/F on conversion and selectivity to maleic anhydride for oxidation of butane.

●○; (VO)₂P₂O₇, ■□; β -VOPO₄.

Reaction conditions; 440°C, butane 1.5%, O₂ 17%.

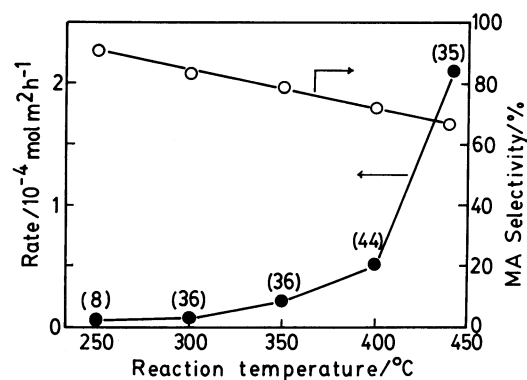


Fig. 7. Effect of reaction temperature on rate and selectivity for oxidation of butane over (VO)₂P₂O₇.

Reaction conditions; butane 1.5%, O₂ 17%.

Figures in parentheses are % conversions.

90% at 250°C.

The effect of the valence of vanadium on the catalytic properties was examined using catalysts which were prereduced by H₂. Prior to the reaction, β -VOPO₄ (catalyst 3) and X₁ were reduced with H₂ in a closed circulation system (200 cm³) at 400°C until the average

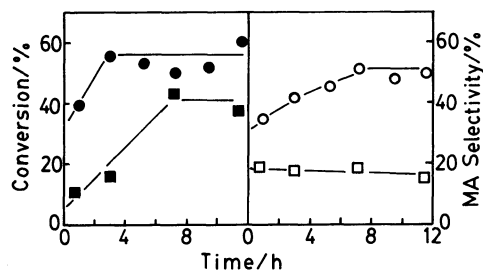


Fig. 8. Variation of activity and selectivity for oxidation of butane over reduced catalysts at 440°C with reaction time.

Reaction conditions; butane 1.5%, O₂ 17%, W/F = $0.67 \times 10^3 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$.

●○; reduced X₁, ■□; reduced β -VOPO₄.

valence of vanadium became four. After the treatment, the structure of β -VOPO₄ and X₁ changed to amorphous. As shown in Fig. 8, the activity increased with the reaction time for both catalysts and became constant at later stage. The rates as well as the selectivity at the steady state were comparable with those of corresponding unreduced catalysts. After the reaction, the reduced β -VOPO₄ showed very weak peaks corresponding to β -VOPO₄ and the reduced X₁ showed XRD peaks corresponding to α -VOPO₄ and (VO)₂P₂O₇.

Discussion

1. *Structure of V-P Oxides with P/V=1.* Several structures have been reported for crystalline phases of V-P mixed oxide catalysts with a P/V ratio close to unity. These phases have recently been reviewed by Delmon and Hodnett.²⁴ Among them, only α -VOPO₄, β -VOPO₄, and (VO)₂P₂O₇ are structures which were determined by XRD analyses of single crystals.

The phases which have been claimed to be efficient catalysts for the selective oxidation of butane to MA are, for example, phase X of ICI¹² and B phase of Chevron.¹³ The XRD powder patterns of X and B closely resemble those of α -VOPO₄ and (VO)₂P₂O₇, respectively. The phases X₁ and X₂ showed XRD patterns very similar to β^* phase reported by Delmon

and Hodnett^{8,24,25} and to B' phase of ICI,²⁶ respectively. Therefore, so far there have been reported five phases of V-P mixed oxide catalysts (P/V=1), i. e., α -VOPO₄, β -VOPO₄, (VO)₂P₂O₇ (=B phase), X₁ (= β^* phase), and X₂ (=B' phase). However, it must be kept in mind that catalysts showing similar XRD patterns are often different in crystallinity and purity and sometimes exhibit quite different activity and selectivity.

2. *Preparation of Single Crystalline Phases.* The preparation processes of the V-P oxides studied in the present work (Tables 2 and 3) are summarized in Fig. 9. As discussed below, these results demonstrate that the factors investigated, i. e., the kind of precursors, the heating rate, the temperature of calcination, and the atmosphere of calcination, are all important factors in determining the resultant structure of catalysts.

2.1 *Calcination in the Oxidizing Atmosphere:* First of all, it is noteworthy that α - and β -VOPO₄ were respectively formed as single phases (judged from XRD powder patterns), by controlling the heating rate. Trifiro *et al.* reported that α -VOPO₄ was transformed to β -VOPO₄ when α -VOPO₄ was heated for a prolonged period at a high temperature,²¹ so that β is likely the more stable phase at high temperatures. Bordes and Courtine¹⁵ reported only the formation of β -VOPO₄ by the calcination of P-I in O₂. However, the present study has revealed that α -VOPO₄ was exclusively formed when the temperature was raised slowly. It is probable that α -VOPO₄ is the phase which crystallizes readily at lower temperatures and that once α -phase is formed it is not easily transformed to the β -phase.

P-I tended to melt at 400–450°C when it was calcined in O₂; sometimes, the gas flow decreased sharply. In these cases, mixtures of α - and β -phases were often obtained. To avoid this phenomenon, we utilized a wide glass tube and raised the temperature gradually while monitoring the rate of gas flow.

Thus, it is important for the preparation of single crystalline phases to control the rate of temperature rise of the calcination process. Trifiro *et al.*²¹ also indicated that the heating rate had a significant influence

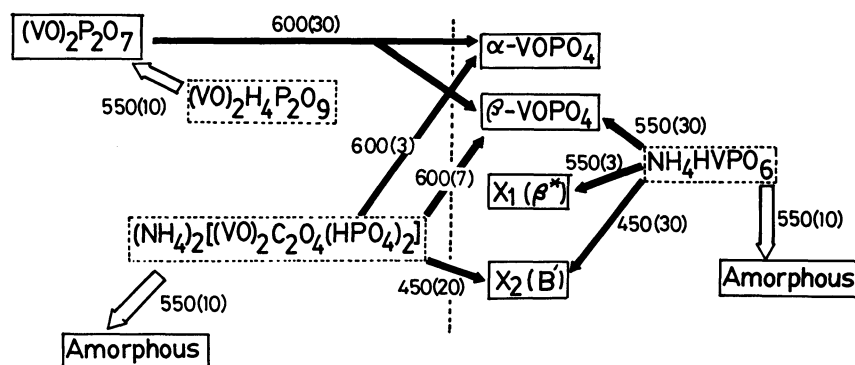


Fig. 9. Preparation processes of V-P oxides.

➡; Calcination in O₂, ⇌; Calcination in N₂.

Figures attached to arrows are calcination temperature and are heating rate (°C min⁻¹, in parentheses).

on the resultant phase.

From P-II (in which vanadium was pentavalent), β -VOPO₄, X₁, and X₂ were respectively obtained by controlling the calcination temperature and the heating rate (Table 2). These results are different from those of Bordes and Courtine¹⁵ who reported the formation of α -VOPO₄. Probably, the detailed conditions of the preparation were different, although they are not described in their paper. X₁ and X₂ crystallized at lower temperatures and were transformed into β -VOPO₄ when calcined at high temperatures. As described above, the X₁ phase showed a XRD pattern similar to the β^* phase which Delmon and Hodnett obtained as mixtures with other phases. They speculated that vanadium in this phase was quadrivalent on the basis of the fact that the fraction of the β^* phase and the average valence state of vanadium changed somewhat in parallel with the calcination time. However, the X₁ phase ($=\beta^*$), which was obtained almost as a single-crystalline phase, has vanadium(V) as determined by redox titration. Although the structures of X₁ and X₂ are not known, it appears probable that they are heteropoly acids with a similar structure (if their solubility in water and the acidic nature of their solutions are considered).

P-III formed mainly (VO)₂P₂O₇ by calcination in air; vanadium (IV) was only partially oxidized to vanadium (V) in contrast to P-I. As described below, due to a similarity in structure, P-III is easily transformed to (VO)₂P₂O₇. This easy transformation may be the reason why the oxidation of vanadium(IV) took place to a much smaller extent than P-I. By calcination at high temperatures, oxidation proceeded progressively to form β -VOPO₄ or X₁. Therefore, it is necessary for a preparation of pure (VO)₂P₂O₇ to calcine P-III in the absence of O₂.

2.2 Calcination in the N₂ Flow: The average oxidation states of vanadium in the amorphous phases which were obtained by calcination in N₂ of P-I and P-III were less than four, presumably due to the reduction of catalyst by the NH₃ present in the precursors. Bordes and Courtine¹⁵ reported the formation of (VO)₂P₂O₇ from P-I. As described above, the phase formed by the calcination of P-I sensitively varies depending on the calcination conditions.

P-III was transformed into (VO)₂P₂O₇ while keeping the valence of vanadium. This is because there was neither a reducing reagent like NH₃ nor an oxidizing reagent. As far as XRD is concerned, (VO)₂P₂O₇, thus formed, was pure. According to the structure of P-III determined recently by Torardi and Cababrese,²⁰ P-III ((VO)₂H₄P₂O₉) and (VO)₂P₂O₇ have a very similar structure (Fig. 10). This may be the reason why apparently pure (VO)₂P₂O₇ was rather easily obtained from P-III.

It was claimed in a patent¹³ that a higher yield of MA was obtained by the recalcination of the catalyst

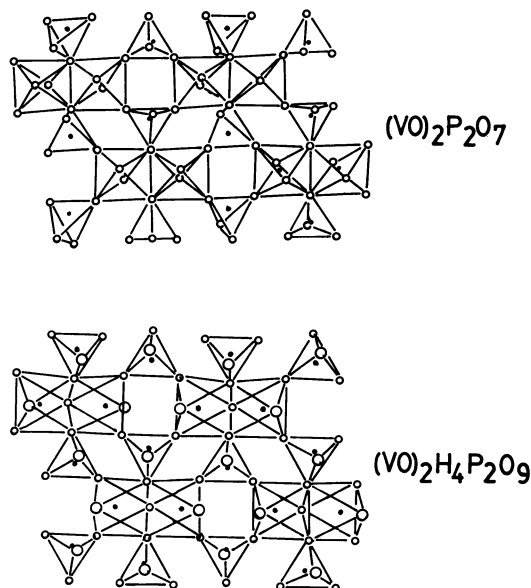


Fig. 10. Structure of (VO)₂P₂O₇ and (VO)₂H₄P₂O₉.²⁰

(probably (VO)₂P₂O₇) in air at a high temperature followed by washing with water and calcination at a lower temperature. The present study (Fig. 1) indicates that amorphous or a less-crystalline phase, contained as an impurity, turned to the X₁ phase by calcination in O₂ and that the X₁ phase, thus formed, was washed out, resulting in a highly crystalline and pure (VO)₂P₂O₇.

2.3 Purity and Crystallinity: Each α - and β -VOPO₄, as well as (VO)₂P₂O₇, prepared in this work by carefully controlling the preparation conditions showed sharp XRD peaks of their corresponding structures. IR spectra also agreed with those reported in the literature. Therefore, the purity and crystallinity of all of these catalysts are considered to be of the highest level among the catalysts used in the preceding studies.

The fact that the oxidation states of vanadium were close to four for (VO)₂P₂O₇ and five for α - and β -VOPO₄ supports this consideration. X₁ and X₂ are likely to have a similar level of purity, as revealed by XRD patterns and IR spectra together with the oxidation state. Furthermore, an XPS analysis showed that the oxidation state of vanadium on the surface was not different from that in the bulk in the cases of β -VOPO₄ and (VO)₂P₂O₇.

3. Efficient Phase for Catalytic Oxidation of Butane to Maleic Anhydride (MA). The catalytic activity and selectivity to MA of each single phase will be phenomenologically discussed. Chevron found a fair correlation between the MA yield and the content of the B phase ($=$ (VO)₂P₂O₇).¹¹ It was claimed that this phase was the efficient phase, although the highest content of the B phase was obtained at P/V=1.2 and the average valence of vanadium was 4.1–4.5.

Later, ICI indicated that phase X ($\approx \alpha$ -VOPO₄) was effective¹² and Delmon's group suggested that the β^* phase was also effective,⁸ while their catalysts were

mixtures. Matsuura suggested that both α -VOPO₄ and (VO)₂P₂O₇ were good catalysts, since the reaction proceeded by the redox cycle between these two phases.⁶⁾ Recently, a patent from Mitsubishi Chemical Industry indicated that their catalysts with P/V=1 exhibited a high MA yield and had a (VO)₂P₂O₇ structure.^{14c)}

In our present study, as discussed above, catalysts contained single crystalline phases. The P/V ratios were all unity and the vanadium valences were close to four or five. Moreover, (VO)₂P₂O₇ was stable and changed little under the reaction conditions. Structural changes of α - and β -VOPO₄ were also negligible. Therefore, it is meaningful to compare the catalytic activity and selectivity of the catalysts as given in Table 5. Table 5 shows that the performance as a catalyst was in the order of (VO)₂P₂O₇ > X₂, X₁ > α -, β -VOPO₄; the selectivity to MA was much better for (VO)₂P₂O₇ (catalysts 9 and 10), while the rate normalized to the surface area was more or less similar. The positions of X₁ and X₂ are not certain, since no single phase of X₁ or X₂ was observed after use for a reaction.

A possible reason for the different performances between (VO)₂P₂O₇ and α -, β -VOPO₄ is the oxidation state of vanadium. However, the prereduced catalysts showed only low selectivities (Fig. 8). Also, the selectivity increased with the reaction time when (VO)₂P₂O₇ was formed after reaction and it maintained a low level when β -VOPO₄ was formed (Fig. 8). Furthermore, amorphous catalysts having low oxidation states of vanadium also showed low selectivities (Table 5). Thus, catalysts containing vanadium(IV) are not always good catalysts. A certain well-defined structure which is stable under the reaction conditions appears to be necessary. Probably, the (VO)₂P₂O₇ catalyst was an efficient catalyst since it consisted of a single crystalline phase in which vanadium(IV) was stable under the reaction conditions. The very high selectivity obtained for (VO)₂P₂O₇ at a low temperature (Fig. 7) may be meaningful since the secondary reactions of MA are not significant in this reaction.

Matsuura suggested that the reaction proceeded by a redox cycle between (VO)₂P₂O₇ and α -VOPO₄.⁶⁾ In the present work for purified (VO)₂P₂O₇, such a redox cycle was not indicated. Nevertheless, the superiority of (VO)₂P₂O₇ is common in the two studies. While Trifiro *et al.*^{9,10)} also reported that the B-phase ($\rightleftharpoons$ (VO)₂P₂O₇) showed a good performance, our results were considerably better at high conversion levels. The purity of (VO)₂P₂O₇ is a possible reason of this difference. Delmon and Hodnett⁸⁾ recently indicated that the β^* phase ($\rightleftharpoons$ X₁) was the efficient phase. The data obtained for the β^* phase were comparable with the X₁ phase in the present study. The X₁ phase was transformed to X₂ and α -VOPO₄ during the reaction (Table 5). If one considers the low selectivity of the α -phase, the pure X₂ phase itself could be a fairly good catalyst.

The variations of activity and selectivity of amor-

phous catalysts 7 and 8 with reaction time are consistent with the concurrent structural changes. When the amorphous catalyst 7 was used as a catalyst, the conversion increased from about 20% (at 3 h) to 60% (after 12 h), and the selectivity to MA decreased from about 30 to about 20%. The steady activity and selectivity were close to those of α -VOPO₄. While the conversion was less than 20% (during 15 h) over the catalyst 8, the selectivity to MA gradually increased with time from 25 to 40% (15 h). This is consistent with the result for X₂.

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