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New Phases in Vanadium Phosphorus Oxides as Butane Selective Oxidation Catalyst

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A new phase, β', has been characterized through a combination of techniques redox titration, paper chromatography, and XRD measurements. The general formula of β'-phase with $(VO)^{2+}(VO)^{3+}_{2n-1}(P_2O_7)^{4-}(PO_4)^{3-}_{2n}$ (n is 1,2,4.8,---,) was performed. The β'-phase is indexed in orthorhombic system with the space group C^5_{2v} similar to that of $(VO)_2(P_2O_7)$. The cell dimensions for the full oxidized β'-phase are given a = 9.751 Å, b = 8.451 Å, and c = 16.968 Å. A topotactic redox reaction undergoes between β'-phase and $(VO)_2P_2O_7$ for the oxidation of butane to maleic anhydride.

Vanadium phosphorus oxides are active and selective catalysts for the oxidation of butane to maleic anhydride. Many patents[1)] and other studies[2)] indicate the best catalysts to have vanadium in the 4+ oxidation state and a P/V ratio of approximately 1. Vanadyl pyrophosphate, $(VO)_2P_2O_7$, is the only well-characterized oxide with this oxidation state and P/V ratio. Recently, Misono et al.[3)] prepared pure $(VO)_2P_2O_7$ and reported it to be an active and selective catalyst for the oxidation of butane to maleic anhydride. According to Bordes and Courtine,[4,5)] there are three phases, α, β, and γ-$(VO)_2P_2O_7$. The XRD patterns of α, β, and γ-$(VO)_2P_2O_7$ are similar, but the diffractograms show some differences in their relative intensities I/I_0 of the main lines. Under oxygen atmosphere, β-$(VO)_2P_2O_7$ is oxidized by a crystallographic shear mechanism to β-$VOPO_4$ which is reduced to β-$(VO)_2P_2O_7$ reversibly. On the other hand, γ-$(VO)_2P_2O_7$ is oxidized topotactically to give γ-$VOPO_4$ which conversely gives back γ-$(VO)_2P_2O_7$ under a nitrogen atmosphere. However, we[6)] found that the stoichiometric $(VO)_2P_2O_7$, found to be β-$(VO)_2P_2O_7$ from the XRD relative intensities I/I_0 of the main lines, is oxidized to β-$VOPO_4$ via β'-phase but β-$(VO)_2P_2O_7$ with excess phosphorus is oxidized only to the stage of the β'-phase. The β'-phase has not yet been characterized even though the results of XRD and oxidation measurements have already been reported.

Vanadyl pyrophosphate with excess phosphate (P/V = 1.1) was prepared in the same way as described in an earlier paper.[6)] High temperature XRD measurement of the sample was carried out in a dried artificial air flow at temperatures from 20 to 800 °C. Under the artificial air, β-$(VO)_2P_2O_7$ is oxidized to the β'-phase at 500 °C and the latter phase does not change anymore up to at least 750 °C. After cooling the sample of the β'-phase to 380 °C, it was transformed to a new phase. Thus it possibly undergoes two modifications, one at high temperature and another

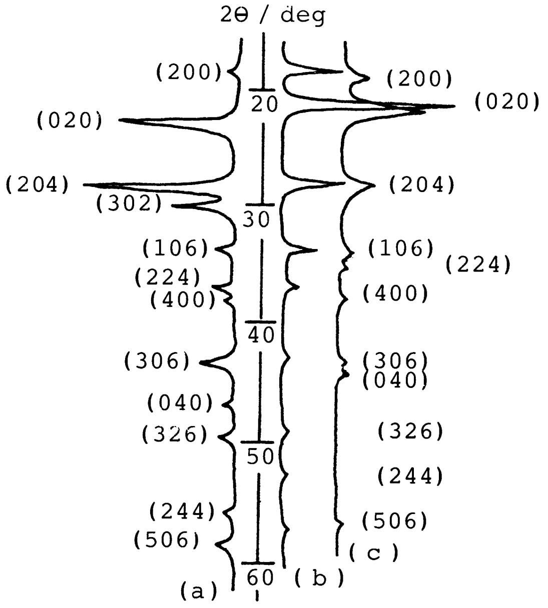


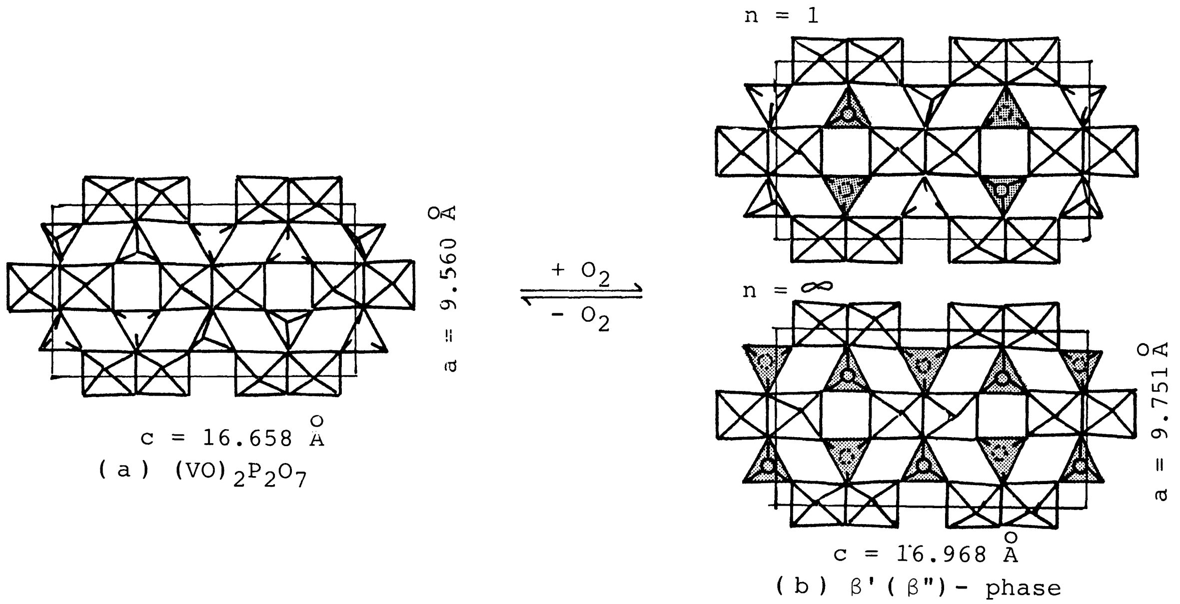
Fig. 1. XRD patterns of vanadium phosphorus oxides: (a) β-$(VO)_2P_2O_7$; (b) β'-phase; (c) β"-phase.

Table 1. XRD Data for β'- and β"-phases, and for β-(VO)$_2$P$_2$)$_7$

	β'-phase			β"-phase			β-$(VO)_2P_2O_7$	
hkl	d calcd / Å	d obsd / Å	I obsd	d calcd / Å	d obsd / Å	I obsd	d obsd / Å	I obsd
200	4.875	4.875	37.5	4.720	4.720	41.7	4.796	17.4
020	4.225	4.230	100.0	4.115	4.115	100.0	3.883	92.4
204	3.200	3.198	39.4	3.150	3.153	40.5	3.153	100.0
302	3.035			2.949			2.983	53.2
106	2.716	2.675	26.0	2.699	2.652	24.0	2.667	22.3
224	2.561			2.500	2.564	21.9	2.449	21.9
400	2.438	2.442	16.1	2.360			2.380	19.4
306	2.133			2.099	2.094	8.6	2.094	30.6
040	2.113	2.113	7.5	2.058	2.058	8.6	1.937	18.0
326	1.904	1.845	8.1	1.870			1.841	17.6
244	1.763	1.725	8.1	1.722			1.644	16.2
506	1.605	1.598	9.8	1.568	1.603	12.3	1.580	20.0
	a = 9.751 Å			a = 9.440 Å			a = 9.560 Å	
	b = 8.451 Å			b = 8.228 Å			b = 7.760 Å	
	c = 16.968 Å			c = 16.919 Å			c = 16.658 Å	
	V = 1398.3 Å^3			V = 1314.1 Å^3			V = 1235.8 Å^3	
	C_{2v}^{5}			C_{2v}^{5}			Pbc2$_1$- C_{2v}^{5}	

at low temperature. The transformation temperature is about 380 °C. We call the high temperature modification a β'-phase and that at low temperature a β"-phase. Exposure of the β"-phase to the air coursed it to become amorphous. It is hygroscopic and dissolves in water. The valence state of vanadium for the β"-phase was determined by means of a redox titration.[7] The valence was between 4.6 and 4.9 which depends upon the oxygen partial pressure. Paper chromatography can distinguish between orthophosphate and pyrophosphate or other more highly condensed phosphate anions.[8] The results of paper chromatography experiments showed both orthophosphate and pyrophosphate to be present in the β"-phase.

Figure 1 shows the XRD patterns of the β'- and β"-phases in comparison with β-$(VO)_2P_2O_7$. The relationship of the XRD patterns among β-$(VO)_2P_2O_7$, β'- and β"-phases are clearly evident. The structure of the β'- and β"-phases thus appear closely related to that of $(VO)_2P_2O_7$. The structure of $(VO)_2P_2O_7$ was previously determined by a single-crystal X-ray diffraction.[9] The crystal structure is orthorhombic and belongs to the space group C_{2v}^5, having lattice constants of a = 9.573 Å, b = 7.725 Å, and c = 16.576 Å. The patterns of the β'- and β"-phases were indexed on the basis of an orthorhombic crystal structure. These data are presented in Table 1. The theoretical values calculated from the cell parameters fit well the experimental values in both phases. A parallel plane to (010) of $(VO)_2P_2O_7$ is shown in Fig.2-a. The layers are held together through V--O = V and P - O - P bonds resulting in the chains of vanadium octahedra sharing opposite corners with the pyrophosphate $(P_2O_7)^{4-}$ groups. Figure 2-b shows a probable structure of the β'-phase as viewed in the (010) plane. The main difference is that half of $(P_2O_7)^{4-}$ in $(VO)_2P_2O_7$ replaces two $(PO_4)^{3-}$ in a perpen-



c = 16.658 Å
(a) $(VO)_2P_2O_7$

c = 16.968 Å
(b) β' (β") - phase

Fig. 2. Comparison of $(VO)_2P_2O_7$ and β'-phase (partially oxidized one and fully oxidized one) viewed in the ac plane. Only half of the each pyrophosphate group is shown and orthophosphate group is shown by shaded tetrahedra.

dicular direction. In the case of fully oxidized state of the β'-phase, total of $(P_2O_7)^{4-}$ in $(VO)_2P_2O_7$ may turn to $(PO_4)^{3-}$. The general chemical formula of the β'-phase can be written as $(VO)^{2+}(VO)^{3+}_{2n-1}(P_2O_7)^{4-}(PO_4)^{3-}_{2n}$ where n is 1, 2, 4, ---, and infinity. The structure of the β"-phase (low temperature modification) may be similar to that of the β'-phase. However, the XRD pattern of the β"-phase shows fewer, broader, and weaker lines than those of the β'-phase. These phenomena may be attributed to a kind of stacking disorder in which vanadyl oxygen and apical phosphate oxygen atoms are each statistically disordered between the two equivalent positions. The fully oxidized β"-phase showed a XRD pattern very similar to that of the X_1-phase reported by Misono <u>et al</u>.$^{3)}$ They suggested that the X_1-phase was moderately effective for n-butane oxidation to maleic anhydride.

The structure of the β'-phase in the ac plane is topologically similar to that of $(VO)_2P_2O_7$ as shown in Fig.2. The similarity of the two structures suggests that oxidation may proceed topotactically. The change from $(P_2O_7)^{4-}$ to two $(PO_4)^{3-}$ in oxidizing $(VO)_2P_2O_7$ to the β'-phase results in a small expansion of b-axis (7.76 Å becomes 8.45 Å) but the other in-plane dimension shows only little change.

We suggest that the topotactic nature of the redox cycle between $(VO)_2P_2O_7$ and the β'-phase is thought to come about more easily; thus the catalytic activity for the oxidation of butane to maleic anhydride is high.

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