New Phases in V–P–O Catalysts and their Role in Oxidation of Butane to Maleic Anhydride

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Three new phases, δ-$VOPO_4$, γ-$VOPO_4$, and γ-$(VO)_2P_2O_7$, have been identified in selective catalysts for butane oxidation, and their role in catalysis is analysed in comparison to butene oxidation into maleic anhydride.

Academic and patent literature has provided much information on V–P–O catalysts for the mild oxidation of butane and the oxidation of butene to maleic anhydride. The chemistry of new preparations yielding V^{4+} precursor 'α-phase' has been studied extensively by Trifirò and co-workers[1] and others.[2,3] However there is still a need for clarification because several known or unknown, crystalline or even 'amorphous' compounds seem to be involved in these reactions: α-$VOPO_4$, β-$VOPO_4$, and 'B-phase', *i.e.* $(VO)_2P_2O_7$, can be identified in the *X*-ray diffraction patterns of the catalysts, sometimes with lines arising from unknown products. Moreover, complexity in this area arises from the influence of the hydrocarbon, the various P/V ratios, the various methods used to obtain the precursor, the various conditions of calcination, the factors

Table 1. Results for heating the V–P–O catalysts under various conditions.

Reactant	Atm.	Approx. temp./°C	Product	Comments
$VOHPO_4\cdot½H_2O$	Air or O_2	450	δ-$VOPO_4$	Layered compound[13]
	O_2	680	γ-$VOPO_4$	See ref. 13
	N_2	500—750	γ-$(VO)_2P_2O_7$	Layered compound;[9a] two steps: $E^{\ddagger}_1 = 21.4$, $E^{\ddagger}_2 = 24.7$ kcal mol^{-1};[a] topotactic reaction
γ-$VOPO_4$	N_2	680—700	γ-$(VO)_2P_2O_7$	Reversible → γ-$VOPO_4$; topotactic[9b] $E'_1 = 36$, $E'_2 = 45$ kcal mol^{-1}
α_{II}-$VOPO_4$	O_2	650	γ-$VOPO_4$	Gives β-$VOPO_4$ at 750 °C
β-$VOPO_4$	N_2	760	β-$(VO)_2P_2O_7$	Reversible → β-$VOPO_4$; crystallographic shear mechanism[4]

[a] 1 cal = 4.184 J.

upon which the surface area depends, the V^{5+}/V^{4+} ratio, and the selectivity. It now appears that the average oxidation state of vanadium must be +4 for the oxidation of butane and +4,+5 for the oxidation of butene.[1—3] No explanation can be given if one disregards the fact that these ions are not free but included in a host matrix which gives to them a selectivity.[4] Therefore our methodology is (i) to determine the phases involved in the catalysts, (ii) to examine their crystal structures, and (iii) to study their reactivity, in order to obtain information on the morphology of the microcrystals, *i.e.* the kind of lattice planes statistically present, which determines the spatial distribution of the atoms at the surface. This should allow us to propose the mechanisms likely to occur in the catalytic process. Such a method has been applied with some success in explaining the role of active supports,[5] while the importance of the surface geometry has been emphasized by Volta, Tatibouet, and others [6—8] with regard to structure-sensitive reactions on oxides.

The precursor 'α-phase' has been identified recently as $VOHPO_4\cdot\frac{1}{2}H_2O$.[9—11] It can be prepared by reduction of V_2O_5 either by strong acids in aqueous medium or by organic reactants,[1—4,12] or by direct reduction of $VOPO_4\cdot 2H_2O$ by isobutyl alcohol.[9] These methods deliver samples with variable crystallinity; the last yields blue hexagonal platelets which allowed the crystal structure to be solved.[10—11] The dehydration of $VOHPO_4\cdot\frac{1}{2}H_2O$ yields three different phases according to the atmosphere and the temperature of decomposition (Table 1): two new polymorphs δ- and γ-$VOPO_4$ and the layered form γ-$(VO)_2P_2O_7$. The reaction yielding γ-$(VO)_2P_2O_7$ has been characterized as topotactic, since pseudomorphic relations with the hydrate have been proved,[9a] and proceeds in two steps with low activation energies. The oxidative dehydration to δ- and then to γ-$VOPO_4$ has also been studied[9b,13] and the successive transitions δ → γ → β-$VOPO_4$ have been observed by differential thermal analysis under oxygen. Under nitrogen, γ-$VOPO_4$ is reduced topotactically to give γ-$(VO)_2P_2O_7$ which conversely gives back γ-$VOPO_4$ under oxygen (Table 1). This redox cycle can be performed many times under isothermal conditions, but the proportion of β-$VOPO_4$ increases with the number of cycles and finally 2β-$VOPO_4$/β-$(VO)_2P_2O_7$ replaces the system 2γ-$VOPO_4$/γ-$(VO)_2P_2O_7$. Consequently the two forms β- and γ-$(VO)_2P_2O_7$ are different although their cell parameters are nearly the same. To summarize, γ-$(VO)_2P_2O_7$ can be identified by its well resolved i.r. spectrum, some *X*-ray diffraction lines in addition to the known $(VO)_2P_2O_7$ pattern[4] (namely 4.14, 3.95, 3.41, and 3.29 Å), and its layered morphology as observed by transmission and scanning electron microscopy.

To return to the catalysts with composition close to P/V = 1 in which the component phases can now be identified, the preparation in organic media favours γ-$VOPO_4$ and γ-$(VO)_2P_2O_7$ being obtained depending upon the calcination conditions, by dehydration of well defined samples of $VOHPO_4\cdot\frac{1}{2}H_2O$. The use of strong acids in aqueous media does not generally allow the oxidation state of vanadium to be controlled and leads to mixtures of the precursor and 'amorphous phase'; on decomposition in air, $(VO)_2P_2O_7$ and/or α-$VOPO_4$, and sometimes β-$VOPO_4$ are obtained. When organic acids such as oxalic or lactic acid are used[2,3] the crystallinity of the samples increases as does the ratio γ/α. These experimental conditions lead to the form α_{II}-$VOPO_4$ ($a = 6.01$, $c = 4.43$ Å)[16] and not α_I-$VOPO_4$ ($a = 6.21$, $c = 4.11$ Å)[4] prepared by dehydration of $VOPO_2\cdot 2H_2O$; α_{II}-$VOPO_4$ is stable upon rehydration and stabilized by the presence of only a small proportion of V^{4+} ions.[17] These forms are related by their reactivity since on heating $VOPO_4\cdot 2H_2O$ in air, α_I-, α_{II}-, γ-, and finally β-$VOPO_4$ are successively formed, although the ranges of stability of α_{II} and γ-$VOPO_4$ are not clearly defined between 600 and 760 °C. While α_I-$VOPO_4$ leads to β-$(VO)_2P_2O_7$ by reduction at 760 °C, α_{II} can yield γ-$(VO)_2P_2O_7$ when heated slowly under nitrogen at 700 °C. However this reaction is not reversible and these samples deliver γ- and β-$VOPO_4$ by reoxidation.

The different behaviour of α-, β-, and γ-phases is related to their crystal structures, the main differences being the presence of single VO_6 octahedra in α- and β-$VOPO_4$, and of pairs of edge-sharing octahedra in the γ-forms and $(VO)_2P_2O_7$.[13—15] Moreover, the planes corresponding to the layers, *i.e.* (010) in $VOHPO_4\cdot\frac{1}{2}H_2O$,[10,11] γ-$VOPO_4$, and γ-$(VO)_2P_2O_7$,[13] are composed of very similar patterns which allow the topotactic character of the transformations to be explained.[9] Very small displacements of the atoms are necessary for the reduction of γ-$VOPO_4$ and the reoxidation of γ-$(VO)_2P_2O_7$, while the reduction of β-$VOPO_4$ into β-$(VO)_2P_2O_7$ involves crystallographic shear planes[4] in order to form the pairs of edge-sharing octahedra from single VO_6 octahedra. The first process is therefore thought to be easier than the second, and to have lower activation energies.[9b]

Application of these considerations to catalysis allows the mild oxidation of butane and the oxidation of butene to maleic anhydride to be differentiated, since the most selective catalysts for the former involve mainly γ-phases while the latter proceeds on β- (or at least α_{II}) catalysts. Further, the presence of the layered form γ-$(VO)_2P_2O_7$ alone is associated with a good selectivity for the mild oxidation of butane. This could mean that the pairs of octahedra which are present at the surface of the (010) layers correspond to the active sites, able to dehydrogenate directly the butane into butadiene, with further cyclization to yield maleic anhydride; a known feature of this reaction is the apparent absence of by-products (except CO_2 and H_2O[1,3]) and this is observed also on the multicomponent $CoMoO_4$–MoO_3–TiO_2 catalyst recently studied.[18] Moreover an explanation for the fact that the mean oxidation state of vanadium is +4 may be found by considering once more the (010) framework; the four vanadium atoms corresponding to the four crystallographic sites[14,15] appear to have partial oxidation states between 3.7 and 4.4. γ-$(VO)_2P_2P_7$ can be understood therefore as a mixed-valence compound, able to act by itself by means of oxidized and/or reduced sites without structural change.[19] In contrast, in the β-$(VO)_2P_2O_7$/β-$VOPO_4$ redox system which is selective for butene oxidation, very few (010) planes are found by transmission electron microscopy, while other cleavage planes such as (100), (011), and (110) are also present. Since both V^{4+}/V^{5+} species are found in selective catalysts,[1,3] this suggests that the allylic adsorption of butene (which requires the presence of V^{5+} sites) does not necessarily proceed on pairs of octahedra, but probably proceeds on the single VO_6 octahedra present at the interface $VOPO_4/(VO)_2P_2O_7$. Such interfaces can be created by crystallographic shear planes while reaching the steady state, or, an equivalent explanation, in $VPO_{4.75}$ considered as an intergrowth structure. This idea has already been proposed by us[4] and has been confirmed recently by *X*-ray photoelectron spectroscopic measurements.[3] The cyclization of the butadiene obtained can proceed in the same way as above, but the variety of sites present on cleavage planes would lead to the formation of the numerous by-products obtained in the oxidation of butene to maleic anhydride. Finally, the presence of β-$VOPO_4$ in used or inactive catalysts for butane oxidation accounts for the loss of selectivity and is due to its greater stability compared with the other forms of $VOPO_4$.

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