Journal of Thermal Analysis, Vol. 30 (1985) 1241—1251

STRUCTURE AND REACTIVITY OF VANADIUM-PHOSPHORUS OXIDES

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The contribution of thermal methods of analysis to the study of the structure and reactivity of vanadium-phosphorus oxides is examined. In particular, data are reported on the solid-state reaction $VOHPO_4 \cdot \frac{1}{2}H_2O \rightarrow (VO)_2P_2O_7 + 2\,H_2O$ for $VOHPO_4 \cdot \frac{1}{2}H_2O$ prepared in different ways, on the redox properties of oxidation and reduction of vanadium for catalysts prepared with different P : V atomic ratios in the range 0.9–1.3, and on the surface properties determined by TPD of catalysts with different P : V ratios. The relationship between these properties and the catalytic properties in the selective oxidation of *n*-butane and but-1-ene is discussed.

Vanadium-phosphorus mixed oxides comprise a very interesting catalytic system for selective oxidation and ammoxidation reactions; these catalysts not only give high yields, but are also able to promote the selective oxidation of different reactants, such as paraffins (*n*-butane), olefins (but-1-ene and butadiene) and alkylaromatics (toluene derivatives) [1, 2]. In all cases the active phase is a pyrophosphate of vanadium(IV) [3–8]. $(VO)_2P_2O_7$ is formed by dehydration of $VOHPO_4 \cdot \frac{1}{2}H_2O$, that can be prepared in different ways [3, 6, 8, 9–12]. However, although the structure is always similar, the catalytic activities of pure $(VO)_2P_2O_7$ phases prepared by different methods differ considerably in particular in selective *n*-butane oxidation [3, 11–14]. This suggests that the activity of these catalysts must be attributed not only to the presence of a particular crystalline compound, but also to the specific nature of that phase, i.e. to the presence of deformations in the crystalline structure.

Since the reaction forming $(VO)_2P_2O_7$ from $VOHPO_4 \cdot \frac{1}{2}H_2O$ is a topotactic one [11, 12, 15], analysis of the transformation can give useful information on the specific nature of the active phase. Therefore, thermal methods of analysis of the solid-state reaction are particularly useful, because they are very sensitive to modifications in the transformation mechanism.

Another peculiarity of these oxides is the possibility of varying the P : V atomic ratio within the range 0.9–1.3 without apparent modification of the $(VO)_2P_2O_7$ structure, even though there is a drastic change of the catalytic activity [13, 16]. Moreover, the content of phosphorus in the catalyst also affects the redox

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properties of the vanadium (as shown by thermogravimetric isothermal measurements under different atmospheres), and it is therefore necessary to correlate the redox properties of these vanadium-phosphorus oxides [16] with their catalytic properties.

Thermal methods of analysis, particularly the temperature-programmed desorption (TPD) technique, are also very useful in the study of the surface energetics of these oxides. Therefore, at the end of this short review on the contribution of thermal analysis methods to the study of the structure and reactivity of vanadium-phosphorus mixed oxides, we shall present an example of how TPD can be used to characterize the reactivity of a vanadium-phosphorus oxide surface [17].

Influence of the method of preparation on the solid-state reaction $VOHPO_4 \cdot \frac{1}{2}H_2O \rightarrow (VO)_2P_2O_7 + 2\,H_2O$.

The precursor of $(VO)_2P_2O_7$ is characterized by a layer structure [11, 12, 18] and is composed of vanadyl hydrogen phosphate layers stacked along the *c* direction. The plane passing through the layers is the (010) plane. $(VO)_2P_2O_7$ is obtained from $VOHPO_4 \cdot \frac{1}{2}H_2O$ by the loss of two water molecules. Its structure [6, 19] consists of coupled pseudo-octahedra (with *trans* vanadyl positions) connected by phosphate tetrahedra; the different planes are connected by asymmetric $V = 0 \ldots V$ bonds and by P—O—P bonds of the pyrophosphate groups.

$VOHPO_4 \cdot \frac{1}{2}H_2O$ can be obtained by different methods:

(i) in aqueous medium by precipitation [4, 5, 20]: V_2O_5 reduction with 37% HCl, addition of o-H_3PO_4, concentration of the solution and addition of water;

(ii) in organic medium: by reduction of V_2O_5 (and subsequent addition of o-H_3PO_4) or of $VOPO_4 \cdot 2H_2O$ with an organic alcohol (such as isobutyl alcohol) [3, 11, 12].

Figure 1 gives X-ray diffraction patterns of $VOHPO_4 \cdot \frac{1}{2}H_2O$ prepared according to methods (i) [sample a(1)] and (ii) {[samples b(1), c(1) and d(1), differing only in the mode of phosphoric acid addition [14]}, and the corresponding $(VO)_2P_2O_7$ obtained after calcination at 670 K in a mixture of 1% *n*-butane/air (reactant mixture in selective *n*-butane oxidation). In all cases, only the X-ray diffraction lines of $VOHPO_4 \cdot \frac{1}{2}H_2O$ and of $(VO)_2P_2O_7$ before and after calcination, respectively, are detected. However, only the sample prepared in an aqueous medium shows X-ray diffraction line intensities which correspond closely to those reported in the literature for the respective crystalline phases both before [a(1)] and after [a(2)] the transformation to $(VO)_2P_2O_7$ [6, 11, 12, 18, 19]. In the catalysts prepared according to method (ii), always both before and after calcination, disorder is present in the plane of layer stacking, as shown by the wider (010) diffraction lines of

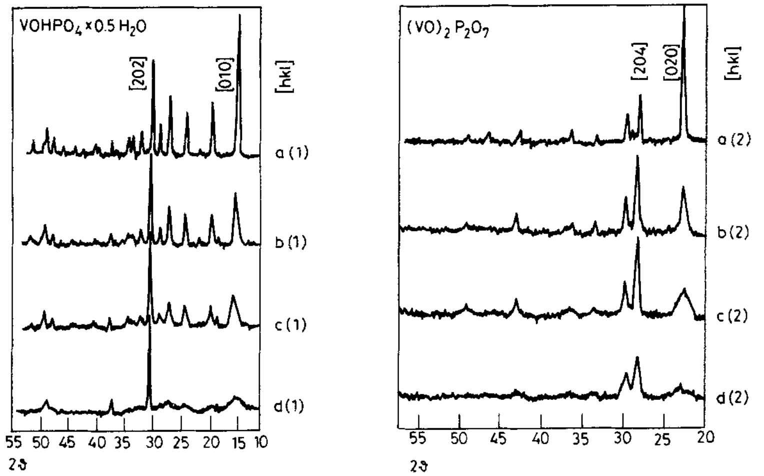


Fig. 1 X-ray diffraction patterns of $VOHPO_4\cdot\frac{1}{2}H_2O$ prepared in aqueous medium (a(1)) and in organic medium varying the modality of phosphoric acid addition (b(1) d(1)) and of corresponding (after dehydratation) $(VO)_2P_2O_7$ phases

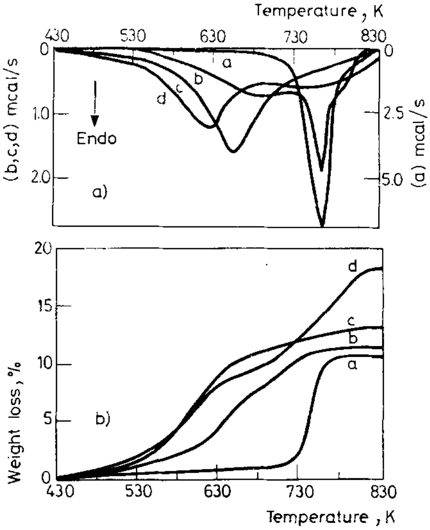


Fig. 2 Differential scanning calorimetry (DSC) and thermogravimetric (TG) analyses of the $VOHPO_4\cdot\frac{1}{2}H_2O \rightarrow (VO)_2P_2O_7 + 2H_2O$ transformation for the same samples of Fig. 1. Scanning rate: 20 deg/min in nitrogen flow

$VOHPO_4\cdot\frac{1}{2}H_2O$ and (020) lines of $(VO)_2P_2O_7$ as compared with the (202) and (204) reflections, respectively [14].

This disorder in the plane of layer stacking drastically modifies the mechanism of the transformation $VOHPO_4\cdot\frac{1}{2}H_2O \rightarrow (VO)_2P_2O_7 + 2\,H_2O$, as shown by the thermal analysis methods (Fig. 2). In the precursor prepared in aqueous medium by precipitation [a(1)], both DSC and TG analyses show that the transformation occurs at high temperatures and in a single step. The weight loss corresponds well to the theoretical weight loss of two water molecules (10.5%). In contrast, for samples prepared in organic medium, the transformation occurs over a broader range of temperatures and starts at much lower temperatures. The total weight is higher than that for the sample prepared in aqueous medium and increases for sample b(1) to sample d(1). This may be explained by the presence of the organic alcohol used as the reacting medium, which remains trapped inside the layered structure of the $VOHPO_4 \cdot \frac{1}{2}H_2O$, as revealed by infrared analysis [14]. Two stages of the transformation can be distinguished in the samples prepared in organic medium; in fact, the DSC curves consist of the superimposition of a sharp peak on a broader peak. The temperature of the maximum of the sharper peak decreases in the sequence b(1)→d(1), in agreement with the increasing disorder of the structure of the samples. Infrared analysis of the catalysts after the maximum of the sharper peak suggests that this peak is associated with the loss of crystallization water, whereas the broader peak is associated with the loss of water formed through the condensation of two hydrogen phosphate groups.

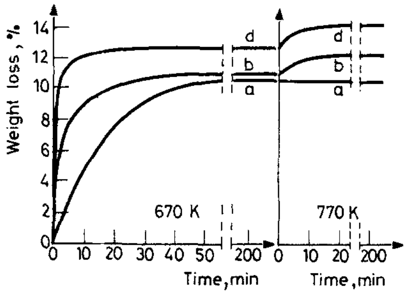


Fig. 3 Isothermal weight loss for the $VOHPO_4 \cdot \frac{1}{2}H_2O \rightarrow (VO)_2P_2O_7 + 2\,H_2O$ transformation at 670 K and after further heating up to 770 K for same samples of Fig. 1

TG isothermal experiments in a nitrogen atmosphere at 670 K (Fig. 3) indicate that all samples lose no further weight after about 50 min. The rate of weight loss increases from sample a(1) to sample d(1), in good agreement with the results from temperature scanning (see Fig. 2b). Infrared analysis [14] after the isothermal experiments indicates that the transformation to vanadyl pyrophosphate is complete. However, in the samples prepared in organic medium, organic alcohol is still present; this can be removed only by further heating at higher temperatures (770 K), as indicated by both TG and infrared analysis. In isothermal experiments in air at 670 K, however, after 50 min the bands due to organic alcohol have completely disappeared in all samples prepared in organic medium. Further, after isothermal calcination at 670 K in a nitrogen atmosphere, the chemical analyses of the samples prepared in organic medium indicate a reduction of the vanadium [6% of V(III) relative to total amount of vanadium found in sample *b*], which does not occur in the sample prepared in aqueous medium. This suggests that in the absence of oxygen the process of alcohol release from the catalyst structure is very slow and that it burns to CO_2 by utilizing lattice oxygen of the catalyst, thereby partially reducing the vanadium of the $(VO)_2P_2O_7$ structure.

The strong differences between the loss of water from the two preparations in aqueous [a(1)] and in organic medium [b(1)→d(1),which occurs in a very short range of temperatures or over a broader range of temperatures and starting at lower temperatures, indicate that the presence of disorder along the plane of stacking of the layers drastically modifies the mechanisms of water loss and condensation of phosphate groups. The increasing degree of disorder along the (010) plane, from sample b(1) to d(1), increases the rate of dehydration. A comparison of samples b(1) and d(1), which have similar surface areas (10 m^2/g and 9 m^2/g, respectively), indicates that the rate of dehydration is strongly affected by the morphology of the catalyst; disorder in the plane of stacking very probably facilitates the expulsion of the water molecules from the catalyst structure.

The different mechanism of transformation to $(VO)_2P_2O_7$ has a considerable influence on the catalytic activity in selective *n*-butane oxidation. In fact, the specific rates of both *n*-butane depletion and maleic anhydryde formation per m^2 of surface area of the catalyst are higher on $(VO)_2P_2O_7$ prepared according to method (ii) than on $(VO)_2P_2O_7$ prepared in aqueous medium [14]. In contrast, no great differences in the specific rate of but-1-ene oxidation are found on $(VO)_2P_2O_7$ phases prepared by the two methods [2, 14]. This considerable influence of the micro-structure of the catalyst on the rate of *n*-butane, but not on the rate of but-1-ene selective oxidation, suggests that the nature of the structure of the active phase mainly influences the first step of selective paraffin oxidation, that is the dehydrogenation of *n*-butane to butenes. These differences suggest that in the catalysts prepared in organic medium some special modifications of the structure are induced by the presence of the alcohol retained between the layers during the calcination stage. The precursor→active phase transformaton is a topotactic reaction which involves the *cis* →*trans* electronic rearrangement of the dimer vanadyl groups and the condensation of two hydrogen phosphates to form the $(VO)_2P_2O_7$ structure without the breaking of V—O—P bonds. During this transformation the presence of organic material between the layers can provoke some local defect structures by steric hindrance or as a consequence of oxygen vacancies caused by the reaction of the alcohol with the lattice oxygen to form carbon oxides. It therefore seems possible to advance a direct correlation between the mechanism of the transformation

$$VOHPO_4 \cdot \tfrac{1}{2}H_2O \text{ (+ trapped organic alcohol)} \rightarrow$$

$$(VO)_2P_2O_7 + 2\,H_2O \; (+CO_2)$$

as evidenced by DSC and TG measurements, and the mechanism of formation of new, very active centers able to activate a paraffin.

Relationship between redox properties and catalytic properties

During the oxidation of 1-butene, it is possible to observe that the reaction temperature has a considerable effect on the distribution of products; more specifically, three different zones can be distinguished, and the main products which are obtained in these zones as the temperature increases are i) butadiene, ii) maleic anhydride and iii) carbon oxides [13].

Analysis of the valence distribution of vanadium in the above-mentioned zones shows the presence of i) V(III) and V(IV), ii)V(IV) and a low content of both V(V) and V(III), and iii) V(IV) and V(V), respectively [13].

This fact suggests that the redox couple V(IV)–V(III) is involved in the formation of butadiene from 1-butene, while the couple V(IV)–V(V) is involved in the formation of maleic anhydride [13]. However, when the surface is excessively oxidized, the maleic anhydride formed is overoxidized to carbon oxides. The oxidation of *n*-butane gives analogous results [16]. It is therefore interesting to correlate the redox properties of the oxidation and reduction of vanadium to the catalytic behavior, i.e. the activity of the catalyst to the rate of reduction of V(IV) and the selectivity (the ratio of the rates of formation and decomposition of maleic anhydride) to the rate of oxidation of V(IV).

It is worth noting that small modifications in the phosphorus content as compared to the stoichiometric ratio P : V = 1.0 strongly affect the catalytic results, and particularly the ratio of the rate of maleic anhydride formation and the rate of formation of carbon oxides.

Moreover, the rate of overall hydrocarbon oxidation is affected by the P : V ratio [3, 16].

Isothermal TG tests using reducing ($He + 2\%\ H_2$) or oxidizing ($N_2 + 20\%\ O_2$) mixtures were therefore used to study the effects of the atomic P : V ratio on the rates of reduction and oxidation of V(IV) (Fig. 4).

Figure 4(a) shows that a deficiency of phosphorus does not modify the rate of V(IV)–V(III) reduction, but does have a strong effect on the rate of V(IV) oxidation to V(V). In contrast, an excess of P only slightly affects the rate of V(V) oxidation,

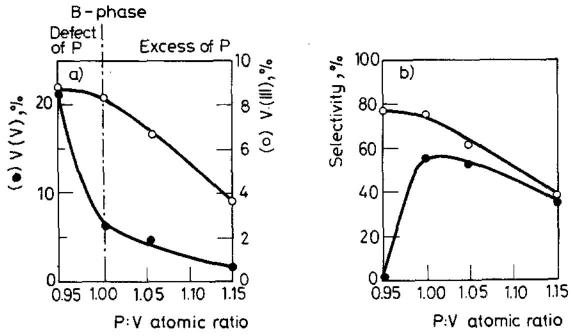
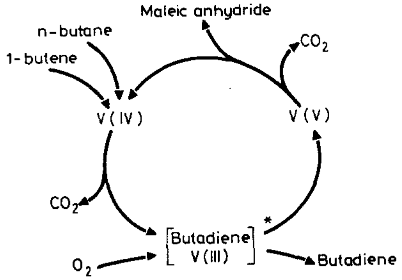


Fig. 4a Rate of vanadium(IV) oxidation at 670 K in air and reduction at 870 K in mixture of 2% H_2/nitrogen as a function of phosphorus: vanadium (P: V) atomic ratio. The rates are expressed as % of V(V) or V(III) respect to total amount of vanadium formed after 30 min.

4b Selectivity in maleic anhydride formation from *n*-butane at 570 K at 10% of conversion (○) and at 80% of conversion (●) as a function of P: V atomic ratio



* Adsorbed phase

Fig. 5 General scheme of the oxidation of *n*-butane and 1-butene to maleic anhydride on vanadium/phosphorus catalysts

but strongly affects the rate of V(IV) reduction. Analysis of the activation energies shows a similar dependence; in particular, the activation energy for the reduction reaction V(IV)→V(III) is the same for the two catalysts with P : V ratios of 0.95 and 1.01 (about 20 kcal/mol), and increases to 27 kcal/mol in the catalyst with P: V = 1.16. The parallel behavior of the activation energies shows that the excess of P decreases not the number of active sites, but rather their reactivity with respect to oxidation and reduction.

On the other hand (Fig. 4b), the catalytic tests show that a deficiency of P (for example in the oxidation of *n*-butane) above all modifies the ratio between the rates of selective oxidation to maleic anhydride and of combustion to carbon oxides, as shown by a comparison of the effect of the P: V ratio on the maleic anhydride selectivity at low and high conversions (at high conversion the effect due to the successive rate of maleic anhydride decomposition increases). However, an excess of P principally affects the rate of hydrocarbon activation. Similar results are obtained in the oxidation of 1-butene [5, 13, 16].

These data allow a general mechanism for the oxidation of C4 hydrocarbons on V—P mixed oxides to be suggested (Fig. 5), providing further evidence of the correlation between the redox properties and the catalytic properties.

Influence of phosphorus on the surface properties

One very useful technique in the investigation of the surface properties of vanadium-phosphorus oxides is temperature-programmed desorption (TPD). This technique allows the nature and energetics of the surface to be analyzed, for example, yielding the desorption energies of different complexes present.

Figure 6 reports the desorption spectra of 1-butene after adsorption at different temperatures on two catalysts prepared with different P : V ratios: 1.0 and 1.4, respectively. Analysis of the individual peaks shows that the products of desorption are, respectively:

(I) 1- and 2-butenes plus butadiene;
(II) furan;
(III) acetic acid and acetic anhydride;
(IV) maleic anhydride.

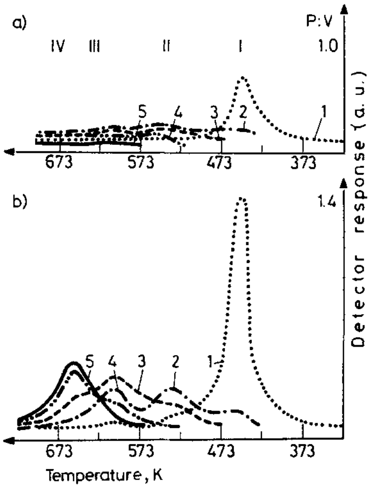


Fig. 6 Temperature programmed desorption (TPD) curves of 1-butene at different temperatures of adsorption on vanadium : phosphorus catalysts with P : V atomic ratio of 1.4 (a) and of 1.0 (b). Adsorption at: 1) 323 K, 2) 423 K, 3) 473 K, 4) 523 K and 5) 573 K

In accordance with what has been shown previously, these data indicate that the excess of phosphorus on the catalyst inhibits the specific centers of maleic anhydride formation. In fact, in the catalyst with a P : V ratio of 1.4, the peaks corresponding to the desorption of maleic anhydride are not present, regardless of the temperature of 1-butene adsorption. Further, these data provide evidence that the formation of maleic anhydride requires activated hydrocarbon adsorption; the maleic anhydride peak is present in the TPD curves only after 1-butene adsorption at temperatures higher than 473 K.

Conclusions

In the study of the structure and reactivity of mixed oxides, such as vanadium-phosphorus oxides, thermal methods of analysis are very useful. In particular, we have demonstrated three aspects in which the contribution of these methods is the determining factor:

i) Studies of the solid-state reaction $VOHPO_4\cdot\frac{1}{2}H_2O\rightarrow(VO)_2P_2O_7+2\,H_2O$ through DSC and scanning and isothermal TG in nitrogen or air provide very sensitive means of establishing variations in the mechanism of water loss which reflects the morphology of the catalyst, the influence of organic alcohol remaining trapped inside the $VOHPO_4\cdot\frac{1}{2}H_2O$ structure during the preparation, and the specific nature of the $(VO)_2P_2O_7$ obtained.

ii) The study, by isothermal TG in different atmospheres, of the redox properties of vanadium (IV), as regards both its oxidation to V(V) and its reduction to V(III); the redox properties are strictly correlated with the catalytic properties.

iii) The study of the surface properties by TPD, which reveals the presence or absence of specific active centers, and the energetics of the surface complex formed, i.e. the decomposition temperature and the activation energy of desorption.

These data therefore indicate some important aspects of the selective oxidation on vanadium-phosphorus oxides, common also to other catalytic systems based on mixed oxides:

i) Not only the presence of a determined phase (or mixture of phases), but even the microcrystalline structure is responsible for the nature of the active centers, and therefore the correlations between structure and catalytic activity on mixed oxides must be considered.

ii) The importance of a particular structure depends too on the nature of the oxidized molecule, even if, for example, 1-butene is an intermediate in the mechanism of selective *n*-butane oxidation. This is clearly related to the rate-limiting step of the two reactions, and therefore to the different natures of the active centers. This reaction (*n*-butane oxidation) on vanadium-phosphorus oxides is in fact an interesting example of a "structure-sensitive reaction".

iii) Different active centers and properties are responsible for the activity and selectivity; for example, on vanadium-phosphorus oxides the activity may be correlated with the presence of particular active centers induced by the presence of organic alcohol during the $VOHPO_4 \cdot \frac{1}{2}H_2O \rightarrow (VO)_2P_2O_7$ transformation (*n*-butane oxidation) or with the rate of reduction of vanadium(IV) (1-butene), whereas the selectivity may be correlated with the rate of oxidation of V(IV) to V(V), i.e. with the different dependences of the rates of formation and decomposition of maleic anhydride on the degree of surface oxidation.

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Zusammenfassung — Der Beitrag thermischer Analysenmethoden zur Untersuchung der Struktur und Reaktivität von Vanadin–Phosphor–Oxiden wird erörtert. Insbesondere werden sich auf die Festkörperreaktion $2VOHPO_4 . 1/2H_2O \rightarrow (VO)_2P_2O_7 + 2H_2O$ für auf verschiedene Weise dargestelltes $VOHPO_4 . 1/2H_2O$, auf die Redox-Eigenschaften von Vanadin in Katalysatoren mit P/V-Atomverhältnissen im Bereich 0,9–1,3 und auf durch TPD bestimmte Oberflächeneigenschaften von Katalysatoren mit unterschiedlichen P/V-Verhältnissen beziehende Angaben gemacht. Zusammenhänge zwischen diesen Eigenschaften und den katalytischen Eigenschaften bei der selektiven Oxydation von n-Butan und N-Buten werden diskutiert.

Резюме — Исследован вклад термических методов анализа в изучение структуры и реакционной способности системы окислов ванадий-фосфор. Приведены, в зависимости от метода получения $VOHPO_4 \cdot 1/2H_2O$, данные для твердотельной реакции $VOHPO_4 \cdot 1/2H_2O \rightarrow (VO)_2P_2O_7 + 2H_2O$, оказывающей влияние на окислительно-восстановительные и поверхностные свойства ванадиевых катализаторов с атомным соотношением P : V в области 0,9 : 1,3. Обсуждена зависимость между этими свойствами катализаторов и их каталитической активностью при селективном окислении н-бутана и 1-бутена.