STRUCTURE AND REACTIVITY OF TITANIA-SUPPORTED OXIDES. PART 1: VANADIUM OXIDE ON TITANIA IN THE SUB- AND SUPER-MONOLAYER REGIONS

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ABSTRACT

Vanadium oxide has been deposited on TiO_2 (washed anatase, $10 \text{ m}^2 \text{g}^{-1}$; Degussa P-25, $55 \pm 3 \text{ m}^2 \text{g}^{-1}$; Eurotitania, $46 \text{ m}^2 \text{g}^{-1}$) by aqueous impregnation of $(\text{NH}_4)_2[\text{VO}(\text{C}_2\text{O}_4)_2]$ and by reaction with VOCl_3 , $\text{VO}(\text{OR})_3 (\text{R}=\text{tBu})$ and $\text{VO}(\text{acac})_2$ in organic solvents. Single applications of the last three reagents form not more than a monolayer of vanadium oxide VO_x , a monolayer being defined as 0.10 wt.% V_2O_5 per m^2 of surface. When less than about four monolayers of VO_x are present, there is in most cases only a single TPR peak: T_{max} values, which increase with V_2O_5 content, are almost independent of the method used but vary slightly with the support ($\text{P-25} < \text{Eurotitania} < \text{washed anatase}$). The 995 cm^{-1} band, characteristic of $\text{V}=\text{O}$ in V_2O_5 , only appears when more than a monolayer of VO_x is present.

In the sub-monolayer region, VO_x is best formulated as an oxohydroxy species bonded to two surface oxygens. As the V_2O_5 content is increased, layers of disordered V_2O_5 are formed on limited areas of the surface, but crystalline V_2O_5 only occurs, probably on top of the disordered V_2O_5 , when the V_2O_5 content exceeds about four monolayers, and takes the form of acicular crystals exposing only planes perpendicular to the a and b axes.

INTRODUCTION

A number of recent papers from our two laboratories have concerned the preparation, characterisation and catalytic properties of monolayers of vanadium oxide (VO_x) on TiO_2 , principally as anatase [1-5]. These have been made chiefly by specific reactions between the vanadium precursor and the OH groups on the TiO_2 surface: precursors used include $\text{VO}(\text{acac})_2$ in solution [2,3] and VOCl_3 both as vapour [4] and in solution [5]. These methods can be applied to give not more than a monolayer of VO_x , this designation being used to denote that the species formed are not well-defined, but are certainly not equivalent to crystalline V_2O_5 . However by repetition of the procedure [2],

layers of VO_x corresponding to more than a monolayer are easily formed.

The traditional procedure for preparing VO_x/TiO_2 catalysts is based on a simple impregnation of the support with an aqueous solution of $(\text{NH}_4)_2[\text{VO}(\text{C}_2\text{O}_4)_2]$ obtained by dissolving NH_4VO_3 in water with oxalic acid. It is unclear at present how the resulting surface species may differ from those obtained with the grafting techniques outlined above. In this paper we use temperature-programmed reduction (TPR) and Laser Raman Spectroscopy (LRS) to characterise the VO_x species formed by both types of method, in both the sub-monolayer and super-monolayer regions. We are therefore in a position to compare the products formed from various precursors and several different supports, and to discuss our findings in the light of those of other groups of workers [6-9]. A particular focus of this work is the transitional region between the single monolayer and the point at which crystalline V_2O_5 appears: this is the range of vanadium concentration equivalent to one to about four monolayers.

EXPERIMENTAL

Preparation of catalysts

The principal physical and chemical properties of the supports employed are shown in Table 1. Anatase samples (Tioxide International plc) were first washed with deionized water by soxhlet extraction and then dried overnight at 120°C ; this significantly decreased the concentrations of the P and K additives (see Table 1), as determined by X-ray fluorescence. Eurotitania is

TABLE 1

Physical and chemical properties of the supports

Designation	% anatase	Surface area/ m^2g^{-1}	Wt.% P	Wt.% K
CLD 1593/1 (as received)	100	10.0	0.38	0.25
CLDD 1593/1 (washed)	"	-	0.18	0.05
CLDD 939 (as received)	"	9.8	0.45	0.28
CLDD 939 (washed)	"	-	0.15	0.05
Degussa P-25 batch A	63	57.6	<0.02	<0.02
batch B	76	55.0	"	"
batch C	68	52.0	"	"
Eurotitania	~100	45.5	-	-

a very pure anatase prepared by Tioxide International plc for the Council of Europe Research Group on Catalysis (EUROCAT). Surface areas were measured by N_2 physisorption, except for batch C of the Degussa P-25 where Ar was used, its cross-sectional area being taken as $16.6\text{\AA}^2$.

For preparation of catalysts by impregnation, 5g of the support was first wetted with doubly-distilled water and dried for 18 h at 120°C . The desired amount of NH_4VO_3 was added to 20 ml of 1M oxalic acid solution, which on heating afforded the deep blue $(NH_4)_2[VO(C_2O_4)_2]$ complex; for high V contents (≥ 14 wt.% V_2O_5), stoichiometric amounts of NH_4VO_3 and oxalic acid were dissolved in 20 ml water. The solution was added to the support, and the water removed by evaporation with continuous stirring. The resulting solid was dried overnight at 120°C and a portion was calcined in flowing air (450°C for 5 h). V contents expressed as wt.% V_2O_5 were in the range 0.4–8.8% for Tioxide anatase and 2–32% for Degussa P-25. Samples made at Brunel University were analysed by Tioxide International plc: samples were dissolved in HF/H_2SO_4 and, after removing the HF, V contents were measured by Inductively Coupled Plasma Spectroscopy to an accuracy of $\pm 0.1\%$. Those prepared at Twente University were analysed by X-ray fluorescence.

The procedure for preparing catalysts using $VOCl_3$ was an improved version of that described before [5]. 5g of Degussa P-25 was placed in a two-necked flask to which an N_2 inlet was attached; after wetting with doubly-distilled water, the TiO_2 was dried under a slow flow of N_2 (150°C for 18 h). A solution of $VOCl_3$ (Aldrich Chemical Co Ltd, 99%) in dry benzene was added, and after fitting a reflux condenser the flask was heated at 70°C for 5 h with stirring. The solid was then filtered under N_2 , washed with pure solvent and dried at 120°C for 1 h. The hot solid was subsequently hydrolysed by passing moist air over it, after which it was dried (120°C , 18 h) and calcined (450°C , 5 h).

In the standard preparations, either 0.2 ml $VOCl_3$ in 50 ml benzene or 0.8 ml $VOCl_3$ in 70 ml benzene was used, the former for the low-area anatase and the latter for high-area supports. If all the vanadium were to deposit on the support, these quantities would give respectively ~ 3.5 and ~ 14 wt.% V_2O_5 : the observed V_2O_5 contents are given in Table 2. In each case only about one-third of the $VOCl_3$ reacts with the support; assuming that the amounts found correspond to the monolayer capacities (see below), we have repeated the whole procedure with Degussa P-25 with a view to obtaining the equivalent of two monolayers, for a third time to obtain either 2.8 or three monolayers (using either 0.6 or 0.8 ml $VOCl_3$) and finally to produce 3.8 monolayers. 0.4 ml $VOCl_3$ was used to prepare a half monolayer.

TABLE 2
Monolayer catalysts

Support	Reactant	Wt.% V_2O_5	Reference
Washed anatase (CLD 939)	$VOCl_3$	0.8	This work
"	$VO(OR)_3$	0.8, 0.9*	"
Washed anatase (CLDD 1593/1)	$VO(acac)_2$	0.79, 0.95*	2a
Eurotitania	$VO(OR)_3$	4.4	This work
Degussa P-25 batch B	$VOCl_3$	3.9, 4.0*	"
"	$VO(OR)_3$	4.0	"
" batch C	$VO(acac)_2$	3.76	12

* Duplicate preparations

Catalysts were also prepared by reaction of $VO(O^iBu)_3$ (prepared from NH_4VO_3 and iBuOH as described by Cartan and Coughlan [10]) with Degussa P-25, to avoid the formation of HCl which might chlorinate unreacted $Ti-OH$ groups. The general procedure was as described for $VOCl_3$, but because of the greater molar volume 2.5 ml of the alkoxide was used in 70 ml toluene with 5g TiO_2 in the standard preparation: the reaction temperature was $75^\circ C$. After filtration the solid was washed, dried and calcined as before. The method was also applied to the CLD939 anatase, using 0.63 ml of $VO(OR)_3$ in 50 ml toluene. The resulting V_2O_5 contents are also given in Table 2, and it appears that again only about 0.3 of the alkoxide reacts with the TiO_2 surface. By subsequent treatments of the single monolayer material (Degussa P-25), we have prepared samples designed to have 1.3, 1.5, 2, 2.3 and 2.5 monolayers, on the assumption that only 0.3 of the alkoxide used in any treatment is actually deposited. Half the standard amount was used to prepare a half-monolayer. The results will be presented and discussed below.

Results are also reported for catalysts prepared by reaction of TiO_2 with vanadyl acetylacetonate $VO(acac)_2$ in either ethanol or toluene as described previously [2] (see Table 2 and below).

Characterisation methods

Procedures for Laser Raman Spectroscopy and for Temperature-Programmed Reduction (TPR) employed at TH Twente have already been described [2,11]; TPR was conducted with a 6% H_2/Ar mixture and a heating rate of $16K\ min^{-1}$. Work at Brunel University employed 6% H_2/N_2 ($40\ cm^3\ min^{-1}$) and a heating rate of $5K\ min^{-1}$. The effect which this difference in heating rate may have on the measured values of T_{max} will be discussed later. Sample weights (18-960 mg)

were adjusted to give approximately equal amounts of H_2 consumed; variation of sample size (85-132 mg) was without significant effect on either T_{max} or V_{H_2} expressed per g of material.

At Brunel University Raman spectra of the samples, as lightly compacted pellets, were excited by Ar^+ 514.5 nm radiation and recorded with a Spex 'Ramalab' spectrometer and an EMI 9862B photomultiplier. Power incident at the sample was ~ 50 mW, and a spectral slit width of 6 cm^{-1} was used.

RESULTS

Estimation of monolayer capacity

Some of the methods we have used were designed to produce a single monolayer of VO_x species on the TiO_2 surface (i.e. the $VOCl_3$, $VO(OR)_3$ and $VO(acac)_2$ methods), while the aqueous impregnation method was intended to be capable of producing more than one monolayer. It is convenient to adopt some definition of monolayer capacity of VO_x species so that V_2O_5 contents of materials based on supports of different surface areas can be compared on the basis of 'number of equivalent monolayers'. In previous publications [1,2,5] we have taken as a basis a single lamella of the V_2O_5 structure, which if laid upon a TiO_2 surface would correspond to 0.145 wt.% V_2O_5 per m^2 of surface. We have then expressed the actual amount of V_2O_5 found by analysis on a support of given area as a fraction of this theoretical monolayer. However it now seems more appropriate to employ an empirical definition of monolayer capacity based on observation. Application of the surface-specific methods noted above to anatase of $\sim 10\text{ m}^2\text{g}^{-1}$ usually leads to a V_2O_5 content of 1.0 ± 0.1 wt.% [see Table 2 and ref.12], i.e. about 70% of a theoretical monolayer based on the structure of V_2O_5 [1]. For the Eurotitania ($45.5\text{ m}^2\text{g}^{-1}$) a single treatment with $VO(OR)_3$ affords 4.4 wt.% V_2O_5 (Table 2), so we may take the figure of 0.10 wt.% V_2O_5 per m^2 as the monolayer capacity for anatase. The various batches of P-25 (Tables 1 and 2) give somewhat lower V_2O_5 contents, i.e. ~ 0.07 wt.% V_2O_5 per m^2 : we are inclined to attribute this either to the possibility that the Degussa P-25 particles comprise a rutile coating on an anatase core or to the existence of surface impurities, especially SiO_2 . In what follows we take 4.0 wt.% V_2O_5 as the monolayer capacity for P-25 of surface area $55 \pm 3\text{ m}^2\text{g}^{-1}$.

Washed anatase as support

Fig. 1 shows the TPR profiles for catalysts containing 0.4-8.8 wt.% V (expressed as V_2O_5) applied by aqueous impregnation to the washed anatase (CLD 939) as described above. Fig. 2 shows the dependence of T_{max} , and Fig. 3 the H_2 consumption per g catalyst, as a function of V_2O_5 content. Fig. 1 also contains the TPR profiles for the support and for pure V_2O_5 measured under the same conditions.

FIGURE 1 TPR profiles for catalysts prepared by aqueous impregnation of washed anatase, and for the support and for pure V_2O_5 . The wt.% V_2O_3 is given for each curve.

FIGURE 2 Dependence of T_{max} on V_2O_5 content for catalysts prepared by (a) aqueous impregnation (open points) and (b) treatment with $VO(acac)_2$ (hatched points) of washed anatase. Circles, first peak; squares, second peak.

FIGURE 3 Dependence of volume of H_2 consumed in TPR on V_2O_5 content for catalysts shown in Fig. 2. Symbols as before; triangles represent total H_2 volume.

FIGURE 4 Raman spectra of catalysts made by aqueous impregnation of washed anatase: the V_2O_5 content (wt.%) is given by each spectrum. Above $\sim 700\text{ cm}^{-1}$, sensitivities are the same; below 700 cm^{-1} they are varied to bring the 640 cm^{-1} band on scale.

FIGURE 5 Raman spectra of low V_2O_5 content catalysts (as in Fig. 4) at higher sensitivity.

The TPR profiles for samples containing 0.4–5.0% V_2O_5 comprise a single peak, the $T_{\max}$ of which increases from about 480°C to 530°C as the V_2O_5 content increases (Fig. 2). This is well below the $T_{\max}$ of the first of the three peaks seen with pure V_2O_5 . At and above 5.4% V_2O_5 the peak splits into two, the $T_{\max}$ for the first being constant at ~530°C, while that for the second continues to increase with V_2O_5 content (Fig. 2). The quantity of H_2 consumed is accurately proportional to the V_2O_5 content (Fig. 3) and corresponds to that required for reduction of V^{5+} to V^{3+} . Approximate manual deconvolution of the split peaks (Fig. 3) appears to show that the first peak attains a constant size after the second starts to appear.

Raman spectra were obtained for the same series of catalysts, as well as for the support and for pure V_2O_5 (Fig. 4). As reported by others [1], bands at 995, 700 and 485 cm^{-1} in V_2O_5 were readily detectable: the first of these is the most intense and is least interfered with by bands due to anatase. Its appearance provides evidence for the existence of $V=O \cdots V$ bonds in the sample in question. For samples containing up to 1.8% V_2O_5 , the portion of the spectrum above 850 cm^{-1} was also run at a higher sensitivity: some of these results are shown in greater detail in Fig. 5. The important feature of these spectra is that the 995 cm^{-1} band is not detectable at V_2O_5 loadings of less than 1.8 wt.%. Similar results have recently been reported by Wachs et al. [6]. From the variation of the intensity of the 995 cm^{-1} band with V_2O_5 content (Fig. 6), it is clearly to be associated with the second and subsequent monolayers, although its intensity does not increase above 5 wt.% V_2O_5 . The

FIGURE 6 Variation in intensities (in cm^{-1}) of 995 cm^{-1} band ($V=O \cdots V$) and 640 cm^{-1} (anatase) bands with V_2O_5 content for catalysts made by aqueous impregnation on washed anatase.

intensity of the bands due to anatase is severely weakened by even the lowest V_2O_5 contents, an effect which has been remarked on before [1] and which is almost certainly due to the Raman scattering process becoming less efficient as the colour deepens with increasing amounts of V_2O_5 . This may also explain why the 995 cm^{-1} band does not continue to increase in intensity. There are no other spectra changes of any significance, and specifically nothing which can be correlated with the development of the second peak in the TPR profiles (Fig. 1).

We now compare the above results for catalysts prepared by aqueous impregnation using $(NH_4)_2[VO(C_2O_4)_2]$ with those obtained with materials made by reacting $VO(acac)_2$ with a similar washed anatase sample (CLDD 1593/1, see Table 1): amounts of V_2O_5 exceeding about 1 wt.% were obtained by reimpregnation using toluene as solvent [2]. The results are also shown in Figs. 2 and 3. The principal difference is that the TPR peak begins to divide at a lower V_2O_5 content than was found with the impregnation catalysts (see Fig. 2). In these cases however the values of T_{max} for the first peak agree well with those for the single peak found before, and values of V_{H_2} consumed are close to those expected for reduction to V^{3+} (Fig. 3). We hope to report further on this difference in a later paper.

Degussa P-25 as support

Three different batches of this support have been used, their surface areas and anatase:rutile ratios being given in Table 1. Two series of catalysts, distinguished by the code letters DP (batch A) and SF (batch B), have been prepared by aqueous impregnation with $(NH_4)_2[VO(C_2O_4)_2]$. Series of catalysts have also been prepared by the $VOCl_3$ and $VO(OR)_3$ methods described above using batch B, and by the $VO(acac)_2$ method [2] with batch C. TPR profiles for the SF series are shown in Fig. 7; those for the DP series were similar in appearance, exhibiting only a single peak up to and including a V_2O_5 content of 9.1%. Values of T_{max} for both series are shown as a function of V_2O_5 content in Fig. 8: the agreement is satisfactory. At very large V_2O_5 contents, equivalent to more than five monolayers, the peak begins to divide (see Figs. 7 and 8): this behaviour is similar to that observed with the low area anatase (Fig. 2) with allowance for the difference in surface area.

We have investigated how monolayers and subsequent layers are formed on the P-25 TiO_2 by the use of V compounds ($VOCl_3$, $VO(OR)_3$, $VO(acac)_2$) which are thought to undergo specific chemical reactions with surface Ti-OH groups. These compounds react with the elimination respectively of HCl, ROH and Hacac [2b]. The pretreatment conditions described above in connection with the first two reagents were designed to remove physisorbed water but not to

FIGURE 7 TPR profiles for catalysts made by aqueous impregnation of Degussa P-25 and for the support. The wt.% V_2O_5 is given for each curve.

FIGURE 8 Dependence of T_{max} on V_2O_5 content for catalysts made by aqueous impregnation of Degussa P-25: hatched points, DP series (batch A); open points, SF series (batch B). Other symbols as in Fig. 2.

dehydroxylate the surface [5]. The exact stoichiometry of the reactions is not known but there is qualitative evidence for the release of HCl in the hydrolysis stage when $VOCl_3$ is the precursor: this and other observations referred to below suggest that each molecule probably reacts with two Ti-OH groups [2b].

We first report our observations with $VOCl_3$ and $VO(OR)_3$. The first treatment of Degussa P-25 (batch B) with either reagent gives 3.9-4.0 % V_2O_5 (Table 2): this we believe corresponds approximately to a monolayer. Although in each case a 3.5-fold excess of reagent was used over that needed for a monolayer, the reaction ceased when the monolayer precursor was formed, so that the first-formed species clearly could not undergo further reaction. However after calcination a second reaction leads to the deposition of about the same further amount of V_2O_5 , as does a third treatment after that (see Fig. 9). The use of

FIGURE 9 Dependence of observed wt.% V_2O_5 on calculated number of monolayers on various supports.

- ▲ $VOCl_3$ method applied to Degussa P-25 (batch B)
- ▼ $VO(OR)_3$ method applied to Degussa P-25 (batch B)
- $VO(OR)_3$ method applied to Eurotitania

half the standard amount of reagent (i.e. a 1.75-fold excess) afforded materials having only 2.6–3.2% V_2O_5 , i.e. 65–80% of a monolayer. The higher figure is given by the alkoxide method. A similar situation arose when we tried to form 1.5 monolayers by a second partial treatment: about the same fraction (0.3) of the reagent used was deposited. Fig. 9 shows how the V_2O_5 contents in fact vary with the intended number of equivalent monolayers calculated on the basis that 0.23 ml $VOCl_3$ (i.e. 0.8 ml/3.5) and 0.71 ml $VO(OR)_3$ (i.e. 2.5 ml/3.5) are required to form monolayers containing 4% V_2O_5 on 5g of Degussa P-25 of surface area $55 \text{ m}^2 \text{ g}^{-1}$, and that a fixed fraction of either reagent used in any treatment (0.3) reacts with the surface. The implications of these findings is that calcination leads to the formation of V species containing one or more OH groups with which further $VOCl_3$ or $VO(OR)_3$ can react. Possible structures will be discussed below. Calcination is thus seen as a necessary step to effect removal of residual organic groups or Cl^- ions which might otherwise limit catalytic activity. We hope to report in a later paper on the changes occurring during calcination.

A similar situation was found [2] with $VO(acac)_2$. Even using a non-polar solvent such as toluene, all variants of the batch adsorption method afforded only 40–50% of the theoretical monolayer quantity of V_2O_5 . Only when the solvent was evaporated to leave all the V on the surface or by dynamic adsorption [2b], or when the material was re-impregnated, could high V_2O_5 contents be obtained. In the latter case the rate of increase of V_2O_5 content

with number of treatments (Fig. 5 of ref. 2) is exactly the same as that in Fig. 9 for the VOCl_3 and VO(OR)_3 methods. It was thought possible that the acetylacetone released on reaction of VO(acac)_2 with the surface Ti-OH groups remained adsorbed, thus interfering with the subsequent process, but the observation (Table 2) that all three methods give about the same V_2O_5 content after a single treatment, and the calculations to be described below, make it less likely that any significant interference by the products actually occurs.

The TPR profiles for materials prepared on Degussa P-25 by the use of either VO(acac)_2 , VOCl_3 or VO(OR)_3 consist of only a single symmetrical peak, the T_{max} of which increases with V_2O_5 content as displayed in Fig. 10. The slopes and intercepts are similar in each case and closely resemble those in Fig. 8 for catalysts made by aqueous impregnation, although the values of T_{max} for the VO(acac)_2 method are slightly higher than the others. We attribute this to the higher heating rate used for materials made by this route: the change in T_{max} with heating rate depends upon the activation energy, which is not known, but from work on V_2O_5 [11] and on CuO [13] we estimate that the correction should be 15-20K. This would bring the results into satisfactory agreement, and we

FIGURE 10 Dependence of T_{max} on V_2O_5 content for catalysts made by various methods on Degussa P-25 and Eurotitania.

◇ VO(acac)_2 method applied to Degussa P-25 (batch C)
Other symbols as in Fig. 9.

FIGURE 11 Dependence of volume of H_2 consumed in TPR on V_2O_5 content for catalysts shown in Figs. 8 and 10.

conclude therefore that there is no essential difference between the surface V species formed by the various procedures.

The corresponding volumes of H_2 consumed per g of catalyst are plotted against V_2O_5 content in Fig. 11. Here however points for the catalysts prepared by aqueous impregnation and by the use of $VO(OR)_3$ lie significantly below the theoretical line for the reduction of V^{5+} to V^{3+} , while points for the other catalysts lie close to it. In the former cases, the composition of the final oxide is about $V_2O_{3.3}$. [The possible significance of this will be discussed below.]

The Laser Raman spectra for some of the catalysts made by the $VO(acac)_2$ method on Degussa P-25 have already been reported (Fig. 1 of ref.2). As with

those shown in Fig. 5 for catalysts made by aqueous impregnation on washed anatase, the sharp line at 995 cm^{-1} characteristic of the $V=O$ stretching vibration in V_2O_5 is absent in the submonolayer region, being barely detectable at a V_2O_5 content of 7.3 wt.% (equivalent to 1.8 monolayers). The decrease in intensity of the 640 cm^{-1} anatase band with increasing V content was also noted. No satisfactory Raman spectra could be obtained with other preparations based on Degussa P-25 because of their dark colour.

Eurotitania as support

A series of catalysts was prepared by the alkoxide method using the Eurotitania support (see Table 1): V_2O_5 contents were between about 2 and 19%. The TPR results are shown in Figs. 10 and 11. $T_{\max}$ again increases linearly with V_2O_5 content in the half to four monolayer region, the intercept (450°C) being a little higher than for the corresponding method in Degussa P-25. The values of V_{H_2} consumed (Fig. 11) are in the main as expected for reduction of V^{5+} to V^{3+} .

DISCUSSION

We begin by summarising the principal features of the TPR results. In the majority of cases, only a single peak is observed up to about the four monolayer point; the exceptions are catalysts prepared by the $VO(acac)_2$ method on washed anatase (Fig. 2), although in these cases the two peaks are only just distinguishable. With both washed anatase and P-25 supports, a second higher-temperature peak is apparent when more than the equivalent of about four monolayers of VO_x are present (Figs. 2 and 8) on catalysts prepared by impregnation.

In all cases where there is only a single peak, the value of $T_{\max}$ increases with V_2O_5 content (Figs. 2, 8 and 10): on the high area supports (Fig. 10) the rates of increase are similar for all preparative methods. There are however significant differences in the intercepts of the plots (i.e. the value of $T_{\max}$ as $[V_2O_5]$ tends to zero). For P-25, these are in the range $\sim 425\text{--}440^\circ\text{C}$; for Eurotitania, it is about 450°C , and for washed anatase $\sim 480^\circ\text{C}$. We conclude that the reducibility of the surface VO_x species is more determined by the support than by the preparation method. Above the four monolayer point, $T_{\max}$ for the first peak ceases to increase (Fig. 2) and its size remains about constant (Fig. 3); $T_{\max}$ for the second peak however continues to increase.

For all catalysts on washed anatase, the total V_{H_2} conforms closely to that expected for reduction of V^{5+} to V^{3+} (Fig. 3). With the high area supports, the situation is a little more complicated (Fig. 11): catalysts made by aqueous impregnation and by the $VO(OR)_3$ method on P-25 show consistently low values of

V_{H_2} , corresponding to a final oxide composition of about $V_2O_{3.3}$. We do not have any explanation for this at the present time.

The differences in T_{max} at low V_2O_5 contents noted above may find their origins in the detailed constitutions of the support surfaces. Residual traces of P and K on the surface of the washed anatase may account for the higher values of T_{max} , in comparison with the lower values on P-25 where these impurities are absent. With unwashed anatase, T_{max} shows a complex dependence on V_2O_5 content, but all values exceed $505^{\circ}C$ [14]. There is however a problem with the P-25 support, in that the precise location of the rutile portion does not seem to be known. It is possible that this exists as a surface coating over an anatase core; if this is so the situation could be summarised as

slightly impure anatase	...	T_{max}	$\sim 480^{\circ}C$
pure anatase (Eurotitania)	...	"	$\sim 450^{\circ}C$
rutile-coated anatase	...	"	$\sim 425-440^{\circ}C$

The parameters describing the TPR peaks (Figs, 2, 3, 8 and 10) provide important clues as to the structure of the surface oxide phases. First, and self-evidently, the first monolayer cannot be represented properly as a single lamella of the V_2O_5 structure as has been suggested [8] and the original concept of structural correspondence between V_2O_5 and anatase [15] cannot be completely correct. This now seems generally agreed [6,7,9]. The probable nature of the surface species will be considered further below. Secondly, there is no marked change in T_{max} at the monolayer point (Fig. 8): we conclude that the general class of structure present in the first monolayer continues to be found as the V_2O_5 content increases up to the equivalent of about four monolayers. Thirdly, the appearance of the second peak above this point (Figs. 2 and 3) probably denotes the formation of a distinct and separate phase which co-exists with the structures formed at lower concentrations. We cannot however completely eliminate the alternative interpretation, namely, of a second phase which is reduced in two stages; the way in which T_{max} for the two peaks changes (Figs. 1 and 2) however suggests that they are not directly connected.

To facilitate further discussion, we shall use the following terminology.

Up to one monolayer	...	surface vanadyl complexes
Two-four monolayers	...	disordered vanadium oxide
Above four monolayers	...	paracrystalline V_2O_5 .

Concerning the species present in the first layer, a detailed EXAFS study [9] has concluded that they are dioxo-vanadium species linked to the surface by two bridging oxygens, and arranged in a disordered fashion. Haber [16] has suggested the following structure (A) on the (010) anatase surface:

This representation is however inadequate on several grounds. The $V=O$ bond order cannot be as high as two, and is more probably about 1.5 [9]; the structure does not have the facility to react with further V precursor to form a second layer, nor does it explain the observation of increased Lewis acidity [8]. For these reasons we prefer the oxohydroxy formulation (B) or a structure (C) in which the electrons are delocalised. It may also explain the absence of the 995 cm^{-1} band below the monolayer point (Fig. 6).

The EXAFS measurements were performed with a very high area ($180\text{ m}^2\text{g}^{-1}$) anatase, and by our criteria the materials used had monolayer coverages of 0.33 and 0.66. It is therefore plausible that the VO_x groups were in the main isolated and randomly disposed on the surface. There is however no reason why at higher V_2O_5 loadings there should not be formed dimers, longer chains, two-dimensional patches and ultimately a complete coverage of the surface at which the $V:Ti$ ratio would be unity. Representation of part of a chain would be as in (D).

It is now not difficult to visualise how further layers might be constructed. The density of Ti^{4+} ions on the (010) anatase surface corresponds to about 6.25 Ti nm^{-2} and at a 1:1 $V:Ti$ ratio of $0.095\text{ wt.}\% V_2O_5$ per m^2 .^{*} This is sufficiently close to the observed values (0.10 ± 0.01) to give confidence in the model. Any dehydroxylation of the surface would however naturally lead to lower V_2O_5

^{*} Reasoning along similar lines van Ommen et al. [2b] calculated $5\text{ wt.}\% V_2O_5$ as the theoretical monolayer for Degussa P-25.

contents where Ti-OH groups are needed to effect the reaction of the V precursor, as would any interference by reaction products (Hacac, HCl etc).

Turning now to the two-four monolayer range, the most plausible scenario is that, on selected parts of the surface, structures such as (B) react with further vanadium precursor to form 'disordered vanadium oxide' growing away from the surface. It is at this stage that the 995 cm^{-1} band first appears, and we suggest that this indicates the presence of $\text{V}=\text{O}\dots\text{V}$ bonds which may exist in a phase other than properly crystalline V_2O_5 .

FIGURE 12(a) Model for surface structure at about the four monolayer point.

FIGURE 12(b) Model for higher V_2O_5 content.

This is shown schematically in Fig. 12(a). During this phase T_{max} increases progressively due to greater difficulty of access to the reducible $\text{V}=\text{O}$ bonds, but the material must be structurally similar to that in the monolayer because there is no abrupt change in T_{max} . This model admits the possibility that the monolayer may not be absolutely complete before the disordered oxide phase begins to be formed.

Above the equivalent of about four monolayers, the amount of 'disordered vanadium oxide' ceases to increase and is replaced by a third phase which we describe as 'paracrystalline V_2O_5 '. It is clearly not the same as normal bulk V_2O_5 in that it is more easily reducible (Fig. 1). We believe that it is formed by extension of the columns of disordered vanadium oxide (see Fig. 12(b)), and it ultimately leads to the very thin acicular crystals observed [17,18] by

electron microscopy growing away from the TiO_2 surface. These crystals will expose chiefly the ac and bc planes, growth occurring in the c direction. Their greater reducibility may be explained by the ease of extraction of O atoms through the a and b planes, with the formation of shear structures [16,19].

This model is an advance upon that proposed recently by Wachs et al. [6], giving a more precise description of possible surface structures. It differs considerably from that of Inomata et al. [8] who clearly believe that it is possible to form a large number of V_2O_5 lamellae parallel to the surface, with some minor variation in thickness.

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