# SnO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>-based catalysts

Nature of surface species and their activity in o-xylene oxidation

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V-Sn-O mixed oxides have been prepared by reaction between tin oxohydrate and vanadium pentoxide at 700 °C. The samples were characterized by means of XPS and UV-VIS diffuse reflectance spectroscopy (DRS). It has been found that different vanadium species formed, the relative amounts of which were a function of the vanadia loading. At a vanadium loading of 4.3 atom%, the SnO<sub>2</sub> surface was covered with a dispersed V<sup>V</sup> species, likely to be in tetrahedral coordination. In addition, V<sup>IV</sup> dispersed in the cassiterite matrix led to the formation of a  $V_x Sn_{1-x}O_2$  solid solution. When the V content is 10 atom%, additional formation of bulk  $V_2O_5$  has been observed. The V<sup>IV</sup> in solid solution modified the electronic properties of the SnO<sub>2</sub>. The calcination temperature also affected the distribution of the vanadium species. Temperatures higher than 700 °C favoured the segregation of SnO<sub>2</sub> and  $V_2O_5$ . The samples were tested in the oxidation of *o*-xylene to phthalic anhydride. It has been found that bulk V<sup>V</sup> oxide is necessary in order to achieve good selectivity, since the V<sup>IV</sup>-doped SnO<sub>2</sub> was not selective to phthalic anhydride. In contrast, the activity was proportional to the overall vanadium content.

Tin oxide, an n-type, wide-gap semiconducting oxide,<sup>1,2</sup> is known to be active in the oxidation of hydrocarbons,<sup>3-5</sup> owing to its ability to release oxygen (forming SnO and suboxides) and its high charge mobility.<sup>6</sup> Its peculiar physicochemical properties also make the Pt/SnO<sub>2</sub> system the most efficient one for the low-temperature recombination of CO and  $O_2$  in  $CO_2$  lasers,<sup>7</sup> and allow its use as a gas sensor for the detection of ammonia, CO and sulfur-containing compounds.<sup>8</sup> Tin oxide can accept guest metal ions, such as V<sup>IV</sup>, Sb<sup>v</sup> and Mo<sup>vi</sup> in its lattice, with formation of substitutional solid solutions, even though this happens in a fairly limited range of metal concentration.<sup>9-17</sup> The V-Sn mixed oxide is particularly interesting. This system is known to act as a catalyst in several oxidation reactions of hydrocarbons, such as the synthesis of acrylic acid from propylene,<sup>15</sup> of benzaldehyde and benzoic acid from toluene,<sup>18</sup> of terephthalic acid from *p*-xylene,<sup>19</sup> of formaldehyde from methanol,<sup>13,20</sup> of nico-tinonitrile from 3-picoline,<sup>16,17</sup> and of ethane to ethene.<sup>21–23</sup> The formation of  $V_x Sn_{1-x} O_2$  solid solutions through replacement of Sn<sup>IV</sup> ions in the cassiterite lattice by V<sup>IV</sup> leads to a modification of the electronic and physicochemical properties of the  $SnO_2$  itself.<sup>12-14,23,24</sup> This was also found to lead to a substantial improvement in the catalytic properties. In the case of ethane oxidative dehydrogenation, the addition of VIV ions up to x = 0.10 led to an increase in catalytic activity.<sup>23</sup>

Formation of the  $V_x Sn_{1-x}O_2$  solid solution can be achieved with different preparation procedures. The most common employs the high-temperature (T > 1000 °C) solid-state reaction between  $SnO_2$  and  $V_2O_5$ , with migration of small amounts of V<sup>IV</sup> ions (up to x = 0.02) inside the  $SnO_2$  lattice. The materials obtained are characterized by a very low surface area ( $<5 \text{ m}^2 \text{ g}^{-1}$ ).<sup>13,14,16</sup> Methods which allow the solid solution to be obtained at a relatively low temperature (and hence materials with a higher surface area, *i.e.* 40 m<sup>2</sup> g<sup>-1</sup>) consist in the solid state reaction at 700 °C, of a mixture between  $V_2O_5$  and tin oxohydrate, or between coprecipitated tin and vanadium oxohydrates.<sup>12,21–23,25</sup> In such cases, the solid solution can be much richer in vanadium (up to x = 0.10) but is not stable, and vanadium oxide segregates at temperatures higher than 700 °C.<sup>23</sup> No methods of preparation lead to the pure solid solution; other phases are formed, *i.e.* amorphous  $V^V$  oxide spread over the surface solution, as well as crystalline  $V_2O_5$  or suboxides.<sup>15,16,18,26</sup> The relative amounts of the different species are a function of the preparation procedure employed, the amount of vanadia loaded and the calcination temperature. These phases affect the catalytic behaviour. In the case of ethane oxidative dehydrogenation, it was found that the  $V^V$ oxide was responsible for the consecutive overoxidation of the ethene formed to CO.<sup>21–23</sup>

In previous work, the V-Sn-O mixed oxides prepared by low-temperature solid-state reaction were characterized, and the reactivity in ethane oxidative dehydrogenation was studied.<sup>21-23</sup> In this work, we complete the characterization of the V-Sn mixed oxide by focussing attention on the surface species. The aim is threefold: (1) to check, by means of X-ray photoelectron spectroscopy (XPS) and UV-VIS diffuse reflectance spectroscopy (DRS), the nature of the vanadium species at the surface of the V-Sn-O system, species that are likely to be involved in the catalysis. (2) To check if the dissolution of  $V^{IV}$  in the SnO<sub>2</sub> affects the electronic features of the material. (3) To study the reactivity of the V-Sn-O system in the oxidation of o-xylene. This system has been compared with the V-Ti-O system, which is industrially employed for the synthesis of phthalic anhydride from o-xylene. The analogies between the two systems are based on crystallographic similarities (one crystallographic form of TiO<sub>2</sub>, rutile, is isostructural with cassiterite), as well as on the nature of vanadium species identified and described in the literature.

## Experimental

The V–Sn–O samples were prepared according to the following procedure.<sup>23</sup> Tin oxohydrate was first precipitated by preparing an ethanol solution of  $\text{SnCl}_4$ , and then by dropping the solution into an aqueous ammoniacal solution, at pH 7. The precipitate, tin oxohydrate, was then filtered, washed and dried at 150 °C. The solid was then mixed with commercial  $V_2O_5$ , in the relative amounts necessary to obtain the final desired Sn/V ratio, and also taking into account the weight loss of the tin oxohydrate when calcined at high temperature. The mixture was then calcined at 700 °C for 3 h. The samples are indicated according to their vanadium content, expressed as V/(V + Sn)% atomic ratio. The samples were dissolved in hot, concentrated  $H_2SO_4$  and analysed by means of volumetric titration according to the procedure described previously.<sup>23</sup> This procedure allows the overall amount of vanadium to be determined, as well as its valence state.

XPS experiments were carried out in an ultra-high vacuum (UHV) VG Scientific ESCALAB 200-C spectrometer. The base pressure in the analysis chamber was kept in the range  $1 \times 10^{-9}$ -5  $\times 10^{-10}$  mbar. The spectra were acquired using an Mg-K $\alpha$  standard source of radiation (1253.6 eV) and the charging effects, due to the non-conductive nature of the samples, were compensated for by referencing the energy scale to the C 1s peak of adventitious carbon, which was assumed to have a binding energy of 284.6 eV. The samples, studied as powders, were analysed without preliminary treatment. The XPS characterization was based on the Sn 3d<sub>5/2</sub>, O 1s and V 2p<sub>3/2</sub> peaks as well as on the valence band region. The O 1s and V 2p<sub>3/2</sub> peaks were acquired together in order to remove the O 1s satellite peaks correctly, which fell in the V 2p region and whose origin lies in the secondary excitation source of Mg-K $\alpha$ .<sup>3.4</sup>

UV-VIS-NIR DRS characterization was carried out using a Perkin-Elmer Lambda 19 spectrometer, equipped with a 60 mm integrating sphere, lined with barium sulfate. The spectra were recorded in the 200-2500 nm region. The 200-250 nm region, however, is only indicative because results in this region are reproduced with difficulty if recorded with different instruments, and also because of the features of the standard employed. The measurements were made at room temperature. The samples were placed in a quartz suprasil cell and a cell filled with white standard (Kodak White Reflectance Standard) was used as the reference. The spectra were recorded by plotting absorbance as a function of wavelength.

Catalytic tests were carried out in a stainless steel flow laboratory reactor at atmospheric pressure. 2 g of catalyst were loaded. In the case of the treated catalyst, the amount loaded was slightly lower owing to the removal of the soluble bulk vanadium oxide. The catalyst was formed in particles with a particle size in the range 0.5-1 mm. The following conditions were employed for o-xylene oxidation: residence time, W/F (catalyst weight/flow rate) 2 g s ml<sup>-1</sup>; feed composition, 1% o-xylene in air; total flow rate, 60 ml of gas min<sup>-1</sup>. At the exit of the reactor, condensable products were collected by cooling and bubbling the reactor outlet stream in dry acetone. The liquid mixture was then analysed by means of gas chromatography, employing a 25 m long, 0.53 mm OV-17 column. The oven temperature was programmed to increase from 80 to 200 °C. Uncondensable gases (CO, CO<sub>2</sub>, O<sub>2</sub>) were analysed by means of a packed column filled with Carbosieve S, and the increase in oven temperature was programmed from 40 to 220 °C. The gas chromatograph was a Hewlett Packard 5600, equipped with a thermoconductivity detector (TCD) (for uncondensable gases) and a flame ionisation detector (FID) (for o-xylene, o-tolualdehyde, phthalide and phthalic anhydride).

## Results

# Analysis of samples calcined at 700 °C

Table 1 reports the data relative to the chemical analysis of the samples studied in the present work. Two different vanadium species were identified with this technique, the relative amounts of which are a function of the overall vanadia loading and of the calcination temperature: (i) a  $V^v$  species, that can be dissolved by treatment with a basic solution, and

Table 1 Chemical analysis of the V-Sn-O samples

sample V content	insoluble V <sup>IV</sup>	soluble V <sup>V</sup>
(atom%)	(atom%)	(atom%)
4.3	2.1	2.2
10.0	4.4	6.6

(ii) a  $V^{IV}$  species that is not removed by treatment with a basic solution, and was found to be chemically bound to the matrix by dissolution in the tin oxide.<sup>23</sup> The same treatment with a basic solution was also used to remove the  $V^V$  species selectively and characterize the matrix by spectroscopic techniques. This treatment therefore leaves an amount of vanadium that corresponds to the insoluble  $V^{IV}$  reported in Table 1.

**XPS characterization.** The XPS characterization was started with a preliminary study on the vanadium and tin compounds used for preparation of the samples, in order to obtain reference parameters and to guarantee internal consistency of all results. The necessity for using one's own measurements has also been pointed out by Horvath *et al.*,<sup>27</sup> in particular in reference to the large dispersion of XPS data relative to vanadium oxides. Fig. 1 shows the Sn  $3d_{5/2}$ , the O 1s peaks and the valence band region of the tin oxide compound. The Sn  $3d_{5/2}$  and O 1s peaks are centred at 486.4 and 530.3 eV, respectively (Table 2), in good agreement with the values given



Fig. 1 Photoelectronic emission regions of SnO<sub>2</sub>

 $\label{eq:table_$ 

sample	Sn 3d <sub>5/2</sub> /eV	O 1s/eV	V 2p <sub>3/2</sub> /eV
SnO <sub>2</sub> <sup>a</sup>	486.4 (1.7)	530.3 (1.6)	
$V_2O_5^{a}$		530.2 (1.6)	517.4 (1.4)
Sn <sup>b</sup>	484.7	· · · ·	( )
SnO <sup>c</sup>	486.7		
SnO <sup>, d</sup>	486.4	530.4	
V <sup>e</sup>			511.9
$V_2O_3^f$		530.1	515.7
VO <sub>2</sub> <sup>T</sup>		529.7	515.9
V <sub>2</sub> O <sub>5</sub> <sup>f</sup>		529.8	516.9

Energy scale referred to C 1s = 284.6 eV. FWHM in brackets. <sup>*a*</sup> This work; <sup>*b*</sup> Ref. 70; <sup>*c*</sup> Ref. 28; <sup>*d*</sup> Ref. 29; <sup>*e*</sup> Ref. 71; <sup>*f*</sup> Ref. 33.

in the literature for  $\text{SnO}_2$ .<sup>28-30</sup> The valence band region, also, corresponds in shape to that reported by Lau and Wertheim<sup>31</sup> for tetravalent tin oxide. Analysis in this region makes it possible to distinguish between SnO and  $\text{SnO}_2$ , which otherwise are fairly similar in the core-level binding energies. In addition, the energy separation between the most intense feature in the valence band and the next Sn 4d core peak (not shown in Fig. 1) was found to be 21.3 eV. Comparison with the values of 23.7 and 21.1 eV observed for SnO and SnO<sub>2</sub> respectively,<sup>32</sup> confirms the absence of reduced tin states in the tin oxide compound.

Fig. 2 reports the XPS core spectral region analysed for the vanadium oxide employed in preparing the catalysts, showing the results after removal of the O 1s satellite peaks. The O 1s peak is centred *ca.* 530.2 eV, while the V  $2p_{3/2}$  peak has its maximum at 517.4 eV (Table 2), in agreement with literature data reported for  $V_2O_5$ .<sup>33,34</sup> In the valence band region of



Fig. 2 Photoelectronic emission regions of  $V_2O_5$ . In the O 1s-V 2p region, the effect of the removal of oxygen satellite peaks is shown.

vanadium oxide, also shown in Fig. 2, the absence of the V 3d signal around 1 eV below the Fermi level<sup>33,35,36</sup> confirms the pentavalent oxidation state of vanadium atoms  $(3d^0)$ .

Fig. 3 compares the core spectra acquired for catalysts containing 4.3 and 10.0 atom% of vanadium and for the latter after being subjected to the washing treatment in an aqueous solution of ammonia. Fig. 4 shows the corresponding spectra in the valence-band region. As described previously,<sup>23</sup> this treatment allows the selective removal of the V<sup>v</sup> oxide spread over the matrix, the latter consisting of the V<sub>x</sub>Sn<sub>1-x</sub>O<sub>2</sub> solid



Fig. 3 Comparison between XPS spectra of catalysts with different vanadium content. The washing treatment effects are also shown.



Fig. 4 Comparison of XPS valence bands of catalysts containing different amounts of vanadium before and after the washing treatment

solution, where V<sup>IV</sup> was found to replace part of the Sn<sup>IV</sup> ions in the rutile lattice. The O 1s and Sn  $3d_{5/2}$  peaks correspond well to those recorded for the reference  $SnO_2$  (Table 3), and can be attributed reasonably to the tin oxide matrix. This indicates that the perturbation induced by the presence of vanadium atoms is not strong enough to modify the binding energy of surface Sn 3d electrons. As shown in Table 3, a general increase of the FWHM for all peaks is observed, as may be expected for a multicomponent system where various kinds of interactions between atoms may occur. The V 2p<sub>3/2</sub> peak exhibits a large FWHM, consisting of two components whose intensity ratio is a function of the overall vanadium loading. The first component is centred at ca. 516 eV, and is predominant at low overall vanadia content, while the second one is centred ca. 517 eV, and becomes prevalent in the vanadium-richer catalyst, as shown in Fig. 5 which reports the results of peak fitting. With increasing vanadia loading, the intensities of the tin and oxygen signals decrease.

The washing treatment removes almost completely the signal of vanadium, as shown in Fig. 3, and the oxygen and tin core peak intensities observed for the naked surface of  $SnO_2$  are recovered. The weak component of the  $V 2p_{3/2}$  peak, left after washing can be assigned to the vanadium species that is not removed by the washing treatment, and that is therefore chemically bound to the surface of the matrix.



Fig. 5 Detail of the peak fitting for the 4.3 atom% V (a) and the 10.0 atom% V (b) samples, both calcined at 700  $^\circ C$ 

A more precise analysis of the peak is not possible due to the very weak signal intensity.

UV-VIS-NIR DRS characterization. Fig. 6 reports the spectra relative to the reference compounds: the  $SnO_2$  (obtained by calcination at 700 °C of the tin oxohydrate), SnO, NH<sub>4</sub>VO<sub>3</sub> (commercial from Carlo Erba), the same V<sub>2</sub>O<sub>5</sub> that was employed for the solid-state reaction with the tin oxohydrate (commercial, from Merck), and VO<sub>2</sub> (commercial, from Fluka).

Fig. 7 compares the spectra for the samples containing the 4.3 and 10.0 atom% of vanadium (the spectrum of  $SnO_2$  is also given for reference), while Fig. 8(a) shows the spectra for the same samples treated with the basic solution. The strong absorption of the  $SnO_2$  below 300 nm makes any evaluation of the absorption due to vanadium species in this region very difficult, and consequently it is also difficult to find a complete match with the reference vanadium oxide spectra. Therefore, discussion will be limited to absorptions falling in the region above 300 nm, where no overlapping with absorption due to tin oxides exists. The main features of the spectra of the



Fig. 6 UV-VIS-NIR DRS spectra of reference compounds



Fig. 7 UV–VIS–NIR DRS spectra of the V–Sn–O samples calcined at 700  $^\circ C$  (4.3 and 10.0 atom% V), and of SnO<sub>2</sub> calcined at 700  $^\circ C$ 

Table 3 Binding energy values of the 4.3 atom..% V sample calcined at increasing temperatures, and of the 10.0 atom% V untreated and treated, compared with reference compounds

sample	Sn 3d <sub>5/2</sub> /eV	O 1s/eV	V 2p <sub>3/2</sub> /eV
4.3 atom% V, 700 °C	486.4 (2.0)	530.0 (2.0)	515.6 (2.3)-517.1 (2.3)
4.3 atom% V, 900 °C	486.5 (1.6)	530.5 (1.6)	515.9 (2.0)-517.1 (2.0)
4.3 atom% V, 1000 °C	486.5 (1.9)	530.3 (2.1)	516.1 (2.1)-517.1 (2.2)
10.0 atom% V, 700 °C	486.4 (2.0)	530.2 (2.0)	515.5 (2.2)-517.0 (2.1)
10.0 atom% V, 700 °C, treated	486.4 (1.8)	530.2 (1.7)	≈ 516 (—)
$SnO_{2}$ (this work)	486.4 (1.7)	530.3 (1.6)	
$V_2O_5$ (this work)		530.2 (1.6)	517.4 (1.4)

Energy scale referred to C 1s = 284.6 eV. FWHM in brackets.



Fig. 8 UV-VIS-NIR DRS spectra of the V-Sn-O samples after treatment with  $NH_4OH$  aqueous solution (a), and difference spectra between untreated and treated samples (b)

V-Sn-O samples are the appearance of a relevant tail in the VIS-NIR region (550-1000 nm), an intense signal at 350-360 nm and a weak shoulder at 450-470 nm (this one is better detected in the second derivative spectrum). The intensity of the signals increases with increasing vanadium content.

The analysis of the spectrum of the two samples after treatment with the ammoniacal solution [Fig. 8(a)] allows a clearer correspondence between bands and vanadium species. The washing treatment appeared to affect the two samples differently, except for a reduced absorption at 400-500 nm, common to both samples, as better revealed by the difference between the two spectra before and after treatment [Fig. 8(b)]. In the sample containing 4.3 atom% vanadium, the solubilization treatment leads to a slight decrease in the intensity of the band at 360-370 nm (which however remains very intense), while in the sample containing 10 atom% vanadium, the band at 360-370 nm rather seems to increase in intensity.

Finally, another effect due to the treatment on the sample with 10 atom% V is the remarkable decrease in the intensity of the absorption in the NIR region; this makes more evident the absorption in the 550-1000 nm range.

#### Effect of temperature of calcination

**XPS characterization.** Fig. 9 shows the XPS core spectra acquired for the 4.3 atom% vanadium catalyst calcined at 700, 900 and 1000 °C. No remarkable change in the binding energy and shapes of the Sn  $3d_{5/2}$  and O 1s peaks was found that could be related to sensible chemical state perturbation of tin and oxygen atoms in the matrix at increasing calcination temperature (Table 2). Regardless of the calcination temperature, the V  $2p_{3/2}$  peak still shows the two components centred *ca*. 516 and 517 eV discussed in the previous section. It is interesting to note, however, that increasing the calcination temperature up to 900 °C resulted in a sensible enhancement of the intensity of the high binding energy vanadium component together with a contraction of the energy distance O 1s-V  $2p_{3/2}$ , while the intensity of the oxygen signal did not vary



Fig. 9 Comparison between XPS spectra of catalysts prepared using different calcination temperatures

remarkably. Otherwise, increasing the temperature up to 1000 °C, led to a substantial decrease in the O 1s peak intensity while the vanadium region remained approximately unchanged. Finally, the Sn  $3d_{5/2}$  peak intensity keeps on decreasing as temperature increases.

UV-VIS-NIR DRS characterization. The effect of the calcination temperature on the sample containing 4.3 atom% vanadium is shown in Fig. 10. The following effects can be observed: (i) the absorbance in the 550-1000 nm region is now replaced by a higher overall absorption in the UV-VIS-NIR region; (ii) the 270-280 and 350-370 nm bands originally present in the sample at 700 °C are left, but the former shifts progressively towards higher wavelength (300 nm) with



Fig. 10 UV-VIS-NIR DRS spectra of the 4.3 atom% V sample after calcination at 700, 900 and 1000  $^{\circ}C$ 



Fig. 11 *o*-Xylene conversion ( $\blacktriangle$ ), yield to phthalic anhydride ( $\diamondsuit$ ), yield to *o*-tolualdehyde ( $\bigcirc$ ), yield to phthalide ( $\triangledown$ ), yield to CO( $\bigstar$ ) and yield to CO<sub>2</sub> ( $\square$ ) as functions of the reaction temperature. Catalyst 4.3 atom% V.

increasing calcination temperature. The band at 410-450 nm is replaced by two weak but more resolved peaks, at 430 and 480 nm, after calcination at 900 °C. At 1000 °C the band is instead broader and similar to that observed at 700 °C.



Fig. 12 Conversion of *o*-xylene as a function of the reaction temperature on the 4.3 atom% V-Sn-O catalyst ( $\blacktriangle$ ), and on the same catalyst after treatment with the NH<sub>4</sub>OH solution ( $\blacklozenge$ ) and of SnO<sub>2</sub> ( $\bigcirc$ )



Fig. 13 Selectivity to phthalic anhydride as a function of the oxylene conversion. Symbols as in Fig. 12.

### Reactivity in o-xylene oxidation

The sample containing the 4.3 atom% vanadium was employed as the catalyst for the gas-phase oxidation of oxylene to phthalic anhydride. The trends of the o-xylene conversion and of the yield to the products as functions of the reaction temperature are given in Fig. 11. The catalyst is remarkably active, reaching total conversion of the o-xylene at 320 °C with W/F 2 g s ml<sup>-1</sup>, and 1% hydrocarbon in air as the feedstock composition. The maximum yield of phthalic anhydride is 52%, which is lower than that achieved on industrial  $V_2O_5/TiO_2$  (anatase) catalysts (usually in the range 75-80%). The yield of phthalic anhydride does not reach a maximum, but rather increases over the entire range of oxylene conversion. This corresponds to a constant selectivity. Minor by-products are phthalide and o-tolualdehyde, the formation of which however decreases with increasing temperature and is nil at total o-xylene conversion. Major by-products are carbon oxides.

Fig. 12 compares the *o*-xylene conversion *vs.* temperature plot with that of the same sample after removal of the soluble vanadium oxide, and of pure  $\text{SnO}_2$  as well. The tin oxide is itself active in the *o*-xylene oxidation; however, the addition of V<sup>IV</sup> with formation of the  $V_x \text{Sn}_{1-x} O_2$  solid solution (treated catalyst) leads to a remarkable increase in the activity. Both samples are however less active than the untreated sample.

Other differences are observed by comparing the plots of the selectivity to phthalic anhydride as functions of the oxylene conversion (Fig. 13). The SnO<sub>2</sub> and the treated V-Sn-O catalyst exhibit similar behaviour, with a relatively high initial selectivity at very low conversion, which however falls as phthalic anhydride conversion increases. In contrast, the selectivity of the untreated catalyst is constant over the entire o-xylene conversion range.

# Discussion

The nature of the phases formed by interaction between the vanadium oxide and the tin oxide has been discussed in detail previously .23 It was found that different types of vanadium species are formed in this system, the relative amounts of which are a function of the V: Sn atomic ratio and of the calcination temperature. The following vanadium species were found: (1) a  $V^{V}$  species that can be selectively removed by treating the calcined sample with an ammoniacal solution. This species, referred to as soluble V<sup>v</sup>, is not bound to the tin oxide (which is not dissolved by such a treatment), and is the prevailing one at overall vanadium contents higher than 4-5 atom%. It is present in the form of an amorphous oxide for V contents lower than 20-25%, while for higher amounts, crystalline  $V_2O_5$  also forms. (2) A V<sup>IV</sup> species that is chemically bound to the tin oxide (insoluble  $V^{IV}$ ), and is stabilized by this interaction in the reduced state up to 700 °C. This species is present in a substitutional solid solution in the SnO<sub>2</sub> lattice,  $V_x Sn_{1-x}O_2$ , up to a maximum x value of 0.10. At temperatures higher than 700 °C, a fraction of this species is expelled from the solid solution, and segregates at the surface as bulk  $V_2O_5$ .

### **XPS** characterization

Many spectroscopic studies have been published characterizing the nature of the vanadium species in mixed oxides and in supported vanadium oxide-based catalysts.<sup>27,38-40</sup> Usually, the interaction of vanadium oxides with supports such as alumina, silica, titania and zeolites, leads to modification of its physicochemical features, and XPS analysis has been widely used as a suitable technique to gain information about the valence state of vanadium in fresh and spent catalysts.

With regard to the V-Sn-O system, the only study of characterization by means of XPS has been published by Andersson and Jaras.<sup>17</sup> The catalysts, employed for the oxidation of alkylpyridines, were prepared by sintering  $V_2O_5$ -SnO<sub>2</sub> mixtures at 1250 °C. The authors found that SnO<sub>2</sub> became embedded in the vanadia due to the melting and spreading of the latter at the high calcination temperature. Calcined, unused catalyst was found to contain vanadium only in the form of V<sup>v</sup> [V 2p<sub>3/2</sub> = 516.9 eV] and tin as Sn<sup>IV</sup> [Sn 3d<sub>5/2</sub> = 486.3 eV], while after reaction, a certain extent of both tin and vanadium reduction was found, as indicated by a broadening of the corresponding signals. No effect was described concerning variations in the shape of the vanadium signal or binding energy for different V/Sn ratios in the catalyst.

It is worth mentioning that while in the case of  $\text{SnO}_2$  and  $V_2O_5$  reference oxides no surface charge phenomena were observed during analysis, in the case of our V-Sn-O samples relevant charge phenomena (10-13 eV) were found, which led to a phenomenon of binding energy ( $E_b$ ) shift during data acquisition. This phenomenon indicates considerable modification of the electric behaviour of the tin oxide (both  $\text{SnO}_2$  and  $V_2O_5$  are n-type semiconductors) induced by the presence of vanadium ions in the lattice.

The XPS spectra clearly indicate the presence of two vanadium signals. The published data on reference vanadium compounds<sup>33</sup> indicate the higher binding energy peak (517 eV) as V<sup>V</sup> species and the lower binding energy peak (516 eV) as V<sup>IV</sup> species. The presence of reduced vanadium states does not find clear confirmation in the valence band region (Fig. 4), where no or only very weak signals are observed around 1 eV. This fact could be related, in any case, to the low concentration of V<sup>IV</sup> species in the outer sample layers. Otherwise, following the suggestions of some authors,<sup>17,38</sup> it is possible to hypothesize the formation of an amorphous vanadium oxide phase with intermediate valence state between IV and V, responsible for the observed 516 eV component in the vanadium peak. This interface phase also might possibly contain dissolved Sn.

As demonstrated by the comparison of spectra before and after washing, the V  $2p_{3/2}$  signal component at *ca*. 517 eV can be attributed to the V<sup>V</sup> oxide overlayers spread over the matrix surface, while the component at lower binding energy is related to the vanadium species which chemically interacts with the tin oxide.

#### **UV-VIS-NIR DRS characterization**

**Reference spectra.** The spectrum of SnO is characterized by a wide and intense absorption band covering the VIS–NIR region, followed by two bands at 380 and 240 nm (3.3 and 5.2 eV, respectively). A different position of the 240 nm band was found (255 nm) for a second sample aged in air. Few papers about the optical behaviour of SnO are found in the literature. Semiconductor behaviour with an optical gap of 3.3 eV has been reported.<sup>42</sup> Such a value is similar to the 380 nm band in the present work. The same paper reports the influence of preparation conditions on the band gap, which actually ranges from 2.7 eV (with annealing in N<sub>2</sub>) up to 3.4 eV (annealing in the presence of O<sub>2</sub>).

The  $\text{SnO}_2$  spectra can be unambiguously distinguished from the SnO spectra by the absence of the wide absorption band in the VIS–NIR region. The main feature of  $\text{SnO}_2$ spectra is the strong transition at 360 nm (*ca.* 3.5 eV) (transition from the valence O 2p band to the conduction Sn 4s band).<sup>42,43</sup> A secondary peak can be distinguished whose edge is located at 495 nm (2.5 eV), which is considered by some authors as being due to impurities in the sample,<sup>42</sup> and by others<sup>44</sup> as corresponding to indirect transitions.

VO<sub>2</sub> can occur in two structures:  $\alpha$  (like MoO<sub>2</sub>, semiconducting, below 70 °C), and  $\beta$  (like rutile, conductor, above 70 °C). The room-temperature semiconducting form of VO<sub>2</sub> is characterized by a wide absorption band in the VIS-NIR

region, centred at ca. 1400 nm, associated with an interband d-d transition.<sup>36,45,46</sup> Transition from the semiconductive to the metallic forms can be detected spectroscopically by a redshift of the charge transfer bands of ca. 0.5 eV and the metallic reflectivity in the NIR region.<sup>36,45</sup> Our reference spectrum shows the wide absorption band in the VIS-NIR region, while in the UV region absorption bands are evident at 220, 345 and a shoulder at 430 nm, the first two associated with charge-transfer transitions from the O 2s or O 2p bands to the V 3d band.<sup>36</sup> In vanadyl complexes, the LCT band is reported to fall in the 200-250 nm range.<sup>47-50</sup> Shin et al.<sup>36</sup> reported, for the semiconductive form of  $VO_2$ , an intense band at 3.6 eV (350 nm, the LCT band), and a less intense one at 2.7 eV (460 nm). A less important component occurs at 4.3 eV (290 nm). Slightly different spectra have been reported by other authors, although bands ca. 2.8, 3.5 and 4.1 eV are commonly observed.45,46,51,52

 $V^{V}$  is a d<sup>0</sup> ion, with a distorted octahedral coordination in  $V_2O_5$ . The latter is an n-type semiconductor and is characterized by the optical absorption edge at 570 nm (2.2 eV).<sup>36,53,54</sup> The charge transfer bands (from the O 2p to the V 3d band) are centred at 475 nm (LCT) and, in the UV region, at 330 and 250 nm.<sup>36,45</sup> These two latter bands have been proposed to be due to the surface tetrahedral V<sup>V</sup> species in  $V_2O_5$ .<sup>47</sup> In addition, weak bands are present in the NIR region (at ca. 1000 nm), which correspond to the ionization energy of an oxygen vacancy.<sup>53,55</sup> The background absorption in the VIS-NIR region is rather intense. This is known to be due to the presence of  $V^{IV}$  impurities in the  $V_2O_5$ ,<sup>56</sup> and the absorption is proportional to the amount of reduced vanadium species.<sup>54,55</sup> The attribution of the band at 470 nm is, however, uncertain. Some authors attribute it to the LCT of the octahedral  $V^{V,36,45}$  others to d-d transitions of  $VO^{2+}$ impurities in the  $V_2O_5$  lattice.<sup>47</sup> In the latter case, the LCT band of octahedral  $V^{V}$  would be masked partially by the 330 nm band at 380 nm.<sup>47,57</sup> Some different samples of commercial  $V_2O_5$  were investigated, and no differences in the spectra were found, except for different background levels, due to differences in the amount of VIV impurities, and minor differences in the location of the first maximum. Indeed, the band at 470 nm in  $V_2O_5$  reference compounds is too intense to belong to a d-d transition of V<sup>IV</sup> impurities. For this reason, we prefer to attribute this band to the LCT transition of octahedral  $V^v$ , in agreement with most spectroscopic studies reported in the literature.

In contrast to  $V_2O_5$ , vanadium in ammonium metavanadate is tetrahedrally coordinated. In this case, the maximum of the first charge transfer absorption band (LCT) is shifted from 450–500 nm (in  $V_2O_5$ ) to 330–360 nm. Two further absorption bands are located in the UV region at *ca.* 280 and 220 nm. Metavanadate spectra lack the background absorption shown by the  $V_2O_5$  samples, which is due to the V<sup>IV</sup> impurities.

V-Sn-O spectra. Absorption bands centred at *ca.* 330-370 nm are common to all reference vanadium oxides. Therefore, the most intense band at 350-370 nm could be assigned either to a CT band of octahedral V<sup>V</sup>, or to a tetrahedral V<sup>V</sup> species (in this case the higher energy CT band at 290 nm should be observed as well), or to the LCT band of V<sup>IV</sup> in VO<sub>2</sub>. A more precise assignment will be possible when discussing the spectra of samples treated with the basic solution. The weak absorption band centred at *ca.* 450-460 nm in the V-Sn-O samples can be attributed to the LCT band of octahedral V<sup>V</sup>.

The attribution of the tail in the VIS–NIR region is more difficult. This is different from the absorption in the NIR region of bulk  $VO_2$ . In this region, d–d transitions for  $VO^{2+}$  complexes (770 and 625 nm)<sup>50</sup> are reported to occur. It has also been reported that the relative intensity of the two bands is a function of the symmetry of the octahedral environment

of  $V^{IV}$ . This assignment has been made in previous papers<sup>58,59</sup> for  $V^{IV}$  species chemically interacting with TiO<sub>2</sub>.

Alternatively, the observed absorbance can be interpreted well by assuming an interaction between the 3d electron of the  $V^{IV}$  in the  $V_x Sn_{1-x}O_2$  solid solution and the conduction band of Sn<sup>IV</sup> (5s orbital). This interaction comes from the very similar energies of these levels, as discussed by Pomonis and Vickerman<sup>14</sup> and demonstrated by other authors.<sup>24,60,61</sup> By means of EPR characterization, it was found that the direct interaction between V<sup>IV</sup> 3d<sup>1</sup> and Sn 5s orbitals is more important than the indirect interaction via the nearest oxygen ligands, since the two bands are energetically closer than the 2p orbital of the oxygen. These authors found that for  $nd^1$ transition-metal ions (tmi) in the SnO<sub>2</sub> matrix (in general, for substitutional solutions of tmi in host oxides having the rutile structure, like SnO<sub>2</sub>, TiO<sub>2</sub> and GeO<sub>2</sub>), a superhyperfine interaction of the guest cations with the nearby cations of the matrix (vanadium with tin) due to the transfer of the unpaired electron from the tmi orbital to the empty ns orbital of the neighbouring cations in the host lattice occurred, leading to broad and unresolved ESR spectra. Moreover, it is known that the presence of transition metals acting as impurity sites in host crystal lattices gives rise to local distortions and consequently to modifications in the optical spectra with, for instance, the widening of some bands or their extension towards lower energies.<sup>62,63</sup>

A similar effect on the UV–VIS spectra due to the interaction between neighbouring host and guest cations in a solid solution was found in the case of the Zn–Cu mixed oxide.<sup>64</sup> The dissolution of Cu<sup>1</sup> in ZnO, the former acting as an impurity in ZnO, led to an extension of the absorbance with a tail towards lower energies, owing to the interaction of the 3d orbitals of Cu with Zn 4s.

In conclusion, there is evidence that interaction occurs at an atomic level. This interaction modifies the energy diagram for the 3d bands around the Fermi level, and rationalises the differences observed in the electronic spectra. For instance, this can explain the absence of the broad absorption band in the NIR region with a maximum *ca.* 1600–1700 nm that in VO<sub>2</sub> is typically due to the interband d–d transitions. Moreover, a modification in the value of the energy gap can be expected; an increase in the energy gap might also justify the absence of peaks around 1 eV in the XPS valence band region. Accordingly, Shin *et al.*<sup>36</sup> found correspondences between the energy position of the main reflectance bands between 2 and 10 eV (620–120 nm) and the maximum positions or band edges of the O 2p bands in UPS in the 0–10 eV binding energy region (XPS spectra in the same region are similar).<sup>36,65</sup>

V-Sn-O samples treated with ammoniacal solution. As described previously,<sup>23</sup> treatment of the samples with ammoniacal solution allows the V<sup>V</sup> oxide spread over the  $V_x Sn_{1-x}O_2$  solid solution to be removed selectively. In the samples treated with ammoniacal solution, the intensity of the absorption band at 450-500 nm is reduced. This indicates that this absorption is relative to the species that is removed selectively by the washing treatment, and that it can be assigned to a V<sup>V</sup> species in an octahedral environment, since this absorption is not observed in tetrahedral V<sup>V</sup>.

The other effects are examined separately in the two samples: (1) In the sample containing 4.3 atom% V, the solubilization treatment leads to a decrease in the intensity of the band at 360-370 nm, which, however, remains very intense. This band must therefore be related to the vanadium species that is chemically interacting with the tin oxide, *i.e.* the vanadium in solid solution in the uppermost atomic layers, thus close to the surface. On the basis of the results reported above for reference vanadium oxides, this band can be assigned to octahedral V<sup>IV</sup> in the rutile host lattice. The slight decrease in the intensity also indicates a contribution due to the highenergy CT band of octahedral  $V^v$ , or to the presence of some amount of  $V^v$  in tetrahedral coordination spread over the matrix, which is removed by the solubilization treatment. (2) In the sample containing 10.0 atom% V, the band at 360–370 nm rather seems to increase in intensity. This difference between the samples with 4.3 and 10.0 atom% V can be explained by taking into account that the sample with 10.0 atom% V has a higher amount of V<sup>V</sup> spread over the matrix,<sup>23</sup> organized into bulk V<sub>2</sub>O<sub>5</sub>-like microcrystallites, which may have a masking effect on the V<sup>IV</sup> species in the underlying solid solution. This effect is removed by the washing treatment. This masking effect is not present in the sample containing 4.3 atom% V, owing to the very low amount of soluble V<sup>V</sup> spread over the solid solution surface.

Another effect occurring in the sample with the higher vanadia loading as a consequence of the treatment is the remarkable decrease in the intensity of the absorption band in the NIR region. A tail is left in the 600–1000 nm region, which confirms the previous assignment of this absorption band to the V<sup>IV</sup> species in the solid solution. The decrease in the NIR region may be due to the fact that soluble V<sup>V</sup> oxide (*i.e.*, the one removed selectively by the solubilization treatment) was impure owing to the presence of V<sup>IV</sup> ions. V<sup>IV</sup> impurities in V<sub>2</sub>O<sub>5</sub> are known to be responsible for absorption in this region.<sup>55–57</sup> The same phenomenon is not observed in the 4.3 atom.% V sample, which also did not exhibit such a strong background absorption in the NIR region; this sample, in fact, contains a very low amount of soluble vanadium oxide.

#### Effect of calcination temperature

Temperatures of calcination higher than 700 °C cause changes in the V-Sn-O as developed at 700 °C. The evolution of the XPS spectra can be interpreted well by assuming (i) a surface enrichment in vanadium occurring at 900 °C with the migration of vanadium ions from the bulk to the outermost catalyst layers of the solid solution, and (ii) a high-temperature induced adjustment of the oxygen sublattice with surface segregation of bulk V<sup>V</sup> oxides and recovery of bulk SnO<sub>2</sub> at 1000 °C. Therefore, these data confirm that the solid solution is not stable at temperatures higher than 700 °C,<sup>23</sup> and that the high temperature vanadium migration leads to a situation where the two oxides, V<sub>2</sub>O<sub>5</sub> and SnO<sub>2</sub>, are preferentially segregated. The remarkable lowering in the intensity of the oxygen peak at 1000 °C can be related to the formation of some vanadium oxide phase, possibly containing tin atoms.

With regard to the evolution of the UV-VIS-NIR DRS spectra, the main effects observed are the following: (1) The absorption band in the VIS-NIR region, attributed to a tail of the charge-transfer band of the  $V^{IV}$  species in solid solution, disappears. This suggests that the solid solution is destroyed by calcination at 900 °C. This was indeed the case, as also demonstrated by the results of XRD, FT-IR and chemical analysis previously published,23 and also in agreement with XPS indications, and further supports the assignment of this absorption band to the V<sup>IV</sup> species in  $V_x Sn_{1-x}O_2$ . (2) The overall background absorption in the VIS-NIR region increases progressively. This could be due either to variations in the average particle diameters as a result of sintering phenomena occurring at high temperature (an increase in crystallinity was indeed observed<sup>23</sup>), or to the presence of  $V^{IV}$  defects in the segregated bulk  $V^V$  oxide. This latter hypothesis is confirmed by chemical analysis, which showed that considerable reduction occurred in bulk vanadium oxide at temperatures higher than  $700 \,^{\circ}\text{C}^{23}$  (3) Other changes are related to modifications in the relative intensity of the bands at 270-280 and 350-370 nm, as well as to the appearance of a weak signal at 480 nm. These modifications can occur as a consequence of the redistribution of vanadium species, due to destruction of the solid solution and to segregation of  $V^{V}$ 

species in the form of isolated  $V^{V}$  sites or of microcrystalline  $V_2O_5$ .

In conclusion, spectroscopic data indicate that at 900 °C the destruction of the solid solution leads to the formation of bulk  $V^{V}$  oxide which, however, is impure owing to the presence of  $V^{IV}$  (partly in the form of defective  $V_2O_5$ , partly in the form of isolated tetrahedral sites) and  $SnO_2$ . At 1000 °C, the oxide segregation is complete.

## Reactivity in o-xylene oxidation

Previously, it was found that doping of tin oxide with  $V^{I\!V}$ ions, and the consequent formation of the  $V_x Sn_{1-x}O_2$  solid solution, led to a modification in the reactivity of the tin oxide in the reaction of ethane oxidative dehydrogenation to ethene.23 In the case of the o-xylene oxidation to phthalic anhydride, the addition of vanadium leads to the creation of new active sites. Indeed, the  $V_x Sn_{1-x}O_2$  catalyst (i.e., the treated sample) is much more active than the tin oxide alone, and, in addition, the activation energy changes from ca. 30 kcal mol<sup>-1</sup> to 51 kcal mol<sup>-1</sup>.<sup>†</sup> Also, the distribution of products is different. With pure tin oxide, only traces of phthalic anhydride are formed, owing to both the low activity and the very low selectivity. The addition of vanadium ions increases the yield to phthalic anhydride, as a consequence of increased activity and selectivity. In this case, however, the selectivity is also decreased with increasing o-xylene conversion.

The catalytic performance is further substantially improved in the untreated sample, and thus in the catalyst, which also possesses dispersed V<sup>V</sup> ions on the surface of the solid solution. The activity of the catalyst increases considerably, and the activation energy is now ca. 27 kcal  $mol^{-1}$ . This indicates that the  $V^{V}$  ions are substantially more active than the  $V^{IV}$ ions, owing to both a lower activation energy and an increase in the number of active sites (likely to be due to an increased availability of the active sites in the dispersed vanadium oxide with respect to the VIV ions dissolved in the matrix of the solid solution). The most important effect, however, is on the selectivity, which not only is increased, but also remains high up to high o-xylene conversion. This difference may be attributed to the higher temperature that is needed for the two less active catalysts, which may be responsible for the consecutive combustion of the phthalic anhydride or for the preferred oxidative degradation of the o-xylene itself. Alternatively, it may suggest that the higher ability of the dispersed V<sup>v</sup> ion in furnishing O<sup>2-</sup> with respect to the V<sup>IV</sup> ions stabilized in the rutile matrix, favours the formation of the selective product.66 Similar results were obtained by Madhok<sup>18</sup> for the oxidation of toluene to benzoic acid. The author found that most selective and active V-Sn-O catalysts were those also possessing bulk  $V_2O_5$  or  $V_6O_{13}$ . Reddy<sup>67</sup> also pointed out the importance of having vanadium oxide spread over the SnO<sub>2</sub> surface in order to have active catalysts in methanol oxidation.

In the case of ethane oxidative dehydrogenation,<sup>22,23</sup> it was found that the activity of the vanadium-doped matrix was not affected by the presence of bulk VV oxide. It was proposed that specific sites are needed to activate the C-H bond of the alkane, and that at the high temperature required for this reaction, the activity of bulk V<sup>V</sup> oxide was much lower than that of the solid solution. The major effect however, also in this case, was on the distribution of the products; the presence of bulk  $V^{v}$  oxide on the matrix decreased the selectivity to the product of selective oxidation (ethene), owing to the increased formation of CO. The effect on selectivity was, therefore, the opposite to that observed here for the oxidation of o-xylene, which could be considered as an indication of the different role of the vanadium species with regard to the nature of the kind of hydrocarbon transformation involved, i.e. oxidative dehydrogenation in the synthesis of ethene from ethane vs. oxygen insertion in the synthesis of phthalic anhydride from o-xylene.

Finally, it is interesting to compare the reactivity of these samples with that of the  $V_2O_5/TiO_2$  (rutile) system, possessing 4.4 atom% vanadium and having a surface area of 60 m<sup>2</sup>  $g^{-1}$ .<sup>68,69</sup> The undoped TiO<sub>2</sub> (rutile) was found to be able to activate the alkylaromatic, giving rise, mainly, to CO2. In contrast, TiO<sub>2</sub> in the anatase form was found to be inactive in this reaction. The same difference in reactivity between the two crystallographic forms of titania was found for the ammoxidation of alkylaromatics to aromatic nitriles.68 In addition, the activity of the V<sup>IV</sup>-doped TiO<sub>2</sub> was found to be higher than that of the undoped rutile. The V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst subjected to the washing treatment (to remove the soluble  $V^{v}$  oxide dispersed on the  $V_{x}Ti_{1-x}O_{2}$  solid solution) exhibited a much more marked decrease in selectivity with increasing conversion than the untreated catalyst, analogous to that occurring with the treated V-Sn-O samples  $(V_x Sn_{1-x}O_2 \text{ solid})$ solutions) described here.

Therefore, the  $V_2O_5/TiO_2$  (rutile) and  $V_2O_5/SnO_2$  systems possess several analogies regarding the reactivity towards *o*xylene. In both cases, the presence of V<sup>IV</sup> in solid solution leads to an increase in the catalytic activity with respect to the pure TiO<sub>2</sub> or SnO<sub>2</sub> supports. The selectivity is also slightly increased, but in order to have catalysts able to give high yields at high hydrocarbon conversion, the additional presence of vanadium oxide spread over the rutile structure is necessary.

### Model of the V-Sn-O system

The data reported in the present work make it possible to complete the model of the V-Sn-O system proposed previously.<sup>21-23</sup> Previous studies established the formation of the solid solution, where  $V^{IV}$  replaced tin ions in the cassiterite lattice, and was therefore stabilized against oxidation. The limit of  $V^{IV}$  dissolution at 700 °C was found to be *ca.* 0.10 atoms per atom of tin. The solid solution was not stable at temperatures higher than 700 °C. It was also proposed that in order to obtain a supersaturated solution it is necessary for a solid-state reaction between vanadium ions and tin oxohy-drate to occur.

These results provide more information on the surface species, and on their role in the catalytic selective oxidation of hydrocarbons. The presence of  $V^{IV}$  atoms in  $SnO_2$ , probably substituting for tin atoms in the rutile lattice is confirmed. The electronic interaction between isolated  $V^{IV}$  ions and neighbouring tin atoms leads to modifications in the energy band diagram of the  $SnO_2$  and of  $VO_2$ , as shown by non-negligible variations in the electronic spectra of the compounds prepared. When spread on the surface of the matrix,  $V^V$  oxide microcrystals build up. The features of this vanadium species are very close to those of bulk  $V_2O_5$ , even though indications have been obtained that at the interface between the solid solution and  $V_2O_5$ , vanadium-tin mixed layers are formed, where vanadium may have an intermediate valence state between IV and V.

Calcination temperatures above 700 °C lead to a progressive expulsion of the V<sup>IV</sup> in solid solution, with formation of bulk V<sup>V</sup> oxide which is, however, impure owing to the presence of V<sup>IV</sup> ions, especially at 1000 °C. The dispersion of V<sup>IV</sup> in the rutile matrix leads to an

The dispersion of  $V^{IV}$  in the rutile matrix leads to an enhancement of the catalytic activity of the tin oxide in the oxidation of *o*-xylene to phthalic anhydride. Vanadium oxide spread over the solid solution is, however, the most active and selective species for the formation of phthalic anhydride. In the case of the oxidative dehydrogenation of ethane<sup>23</sup> (a less facile reaction than *o*-xylene oxidation), at the highest temperatures required for alkane activation the reactivity of tin oxide and of the solid solution are comparable.

 $<sup>\</sup>dagger$  cal = 4.184 J.

The V-Sn-O system has several analogies with the V-Ti-O system where TiO<sub>2</sub> has the rutile crystalline structure; also in this case the selectivity to phthalic anhydride at high conversion was guaranteed by the presence of bulk vanadium oxide spread over the  $V_x Ti_{1-x}O_2$  solid solution.

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#### References

- 1 J. L. Jacquemin and G. Bordure, J. Phys. Chem. Solids, 1975, 36, 1081.
- 2 F. J. Arlinghaus, J. Phys. Chem. Solids, 1974, 35, 931.
- R. Burch and E. M. Crabb, Appl. Catal. A: General, 1993, 97, 49. 3
- 4 A. Argent and P. G. Harrison, J. Chem. Soc., Chem. Commun., 1986, 1058.
- P. G. Harrison and B. Maunders, J. Chem. Soc., Faraday Trans. I, 1985, 81, 1311.
- Z. M. Jarzebski, in Oxide Semiconductors, International Series of 6 Monographs in the Science of Solid State, ed. B. R. Pamplin, Pergamon Press, Oxford, 1973, vol. 4.
- 7 R. K. Herz, in Low-Temperature CO Oxidation Catalysts for Long-Life CO2 Lasers, NASA Conf. Publ. 3076, ed. D. R. Schryer and G. B. Hoflund, Washington DC, 1990, p. 21.
- K. Takahata, in Chemical Sensor Technology, ed. T. Seiyama, 8 Elsevier Science, Amsterdam, 1988, vol. 1, p. 39.
- D. Pyke, R. Reid and R. Tilley, J. Chem. Soc., Faraday Trans. 1, 9 1980, 76, 1174.
- 10 F. J. Berry, L. A. Bursill and D. J. Smith, J. Solid State Chem., 1982, 44, 326.
- F. J. Berry, C. Hallett and M. H. Loretto, J. Solid State Chem., 11 1985, 58, 176.
- W. M. H. Sachtler, G. J. H. Dorgelo, J. Fahrenfort and R. J. H. 12 Voorhoeve, Proc. Fourth Int. Congr. Catalysis, Moscow, 1968, p. 454.
- P. Pomonis and J. C. Vickerman, Faraday Discuss. Chem. Soc., 13 1981, **71**, 247.
- P. Pomonis and J. C. Vickerman, J. Catal., 1984, 90, 305. 14
- 15 T. Ono, Y. Nakagawa and Y. Kubokawa, Bull. Chem. Soc. Jpn., 1981, **54**, 343.
- A. Andersson, J. Catal., 1981, 69, 465. 16
- S. L. T. Andersson and S. Jaras, J. Catal., 1980, 64, 51. 17
- K. L. Madhok, React. Kinet. Catal. Lett., 1984, 25, 159. 18
- B. C. Mathur and D. S. Viswanath, J. Catal., 1974, 32, 1. 19
- B. M. Reddy, K. Narsimha, Ch. Sivaraj and P. K. Rao, Appl. 20 Catal., 1989, 55, L1.
- 21 S. Bordoni, F. Cavani, E. Foresti, F. Trifirò, M. P. Kulkarni and M. Koutyrev, in Actas XIII Simposio Iberoamericano de Catalisis, Segovia, Repsol Petroleo, Madrid, 1992, p. 619.
- S. Bordoni, F. Castellani, F. Cavani, F. Trifirò and M. P. Kulk-22 arni, in New Developments in Selective Oxidations II, ed. V. Cortés Corberan and S. Vic Bellon, Elsevier Science, Amsterdam, 1994, p. 93.
- 23 S. Bordoni, F. Castellani, F. Cavani, F. Trifirò and M. Gazzano, J. Chem. Soc., Faraday Trans., 1994, 90, 2981.
- C. Kikuchi, I. Chen, W. H. From and P. B. Dorain, J. Chem. 24 Phys., 1965, 42, 181.
- 25 F. Okada, A. Satsuma, A. Furuta, A. Miyamoto, T. Hattori and Y. Murakami, J. Phys. Chem., 1990, 94, 5900.
- M. Ai, J. Catal., 1975, 40, 318. 26 27 (a) B. Horvath, J. Strutz, J. Geyer-Lippmann and E. G. Horvath,
- Z. Anorg. Allg. Chem., 1981, 483, 181; (b) 193; (c) 205. 28
- H. Willemen, D. F. van de Vondel and G. P. van der Kelen, Inorg. Chim. Acta, 1979, 34, 175.
- 29 A. W. C. Lin, N. R. Armstromg and T. Kuwana, Anal. Chem., 1977, 49, 1228.
- 30 P. R. Moses, L. M. Wier, J. C. Lennox, H. O. Finklea, J. R. Lenhard and R. W. Murray, Anal. Chem., 1978, 50, 576.
- C. L. Lau and G. K. Wertheim, J. Vac. Sci. Technol., 1978, 15, 31 622
- 32 P. M. A. Sherwood, Phys. Rev. B, 1990, 41, 10151.

- G. A. Sawatzky and D. Post, Phys. Rev. B, 1979, 20, 1546. 33
- 34 C. Blaauw, F. Leenhouts, F. van der Woode and G. A. Sawatzky, J. Phys. C, 1976, 8, 129.
- 35 T. Allersma, R. Hakim, T. N. Kennedy and J. D. MacKenzie, J. Chem. Phys., 1967, 46, 154.
- S. Shin, S. Suga, M. Taniguchi, M. Fujisawa, H. Kanzaki, A. 36 Fujimori, H. Daimon, Y. Ueda, K. Kosuge and S. Kachi, Phys. Rev. B, 1990, 41, 4993.
- 37 S. L. T. Andersson, J. Chem. Soc., Faraday Trans. 1, 1979, 75, 1356.
- 38 K. Seshan, H. M. Swaan, R. H. H. Smits, J. G. van Ommen and J. R. H. Ross, in New Developments in Selective Oxidation, ed. G. Centi and F. Trifirò, Elsevier Science, Amsterdam, 1990, p. 505.
- 39 B. Jonson, B. Rebenstorf, R. Larsson, S. L. T. Andersson and S. T. Lundin, J. Chem. Soc. Faraday Trans. 1, 1986, 82, 767.
- 40 P. Meriaudeau and J. Vedrine, Nouv. J. Chim., 1977, 2, 133
- 41 R. Sivaramasubramaniam, M. R. Muhamad and S. Radhakrishna, Phys. Status. Solidi A, 1993, 136, 215.
- J. L. Jacquemin and G. Bordure, J. Phys. Chem. Solids, 1975, 36, 42 1081.
- 43 R. Summitt, J. A. Marley and N. F. Borrelli, J. Phys. Chem. Solids, 1964, 25, 1465.
- F. J. Arlinghaus, J. Phys. Chem. Solids, 1974, 35, 931. 44
- 45 V. G. Mokerov and A. V. Rakov, Sov. Phys. Solid State, 1969, 11, 150.
- L. Ladd and W. Paul, Solid State Commun., 1969, 7, 425. 46
- 47 J. Hanuza, B. Jezowska-Trzebiatowska and W. Oganowski, J. Mol. Catal., 1985, 29, 109.
- J. Selbin and F. Morpugo, J. Inorg. Nucl. Chem., 1965, 27, 673. 48
- C. J. Ballhausen and H. B. Gray, Inorg. Chem., 1962, 1, 111. 49
- 50 J. Selbin, Chem. Rev., 1965, 65, 153.
- 51 H. W. Verleur, A. S. Barker and C. N. Berglund, Phys. Rev., 1968, 172, 788.
- 52 A. Gavini and C. C. Y. Kwan, Phys. Rev. B., 1972, 5, 3138.
- 53 N. Kenny, C. R. Kannewurf and D. H. Whitmore, J. Phys. Chem. Solids, 1966, 27, 1237.
- J. Bullot, P. Cordier, O. Gallais, M. Gauthier and F. Babonneau, J. Non-Cryst. Solids, 1984, **68**, 135. F. Vratny and F. Micale, *Trans. Faraday Soc.*, 1963, **59**, 2747.
- 55
  - T. Allersma, R. Hakim, T. N. Kennedy and J. D. MacKenzie, J. 56 Chem. Phys., 1967, 46, 154.
  - H. So and M. T. Pope, Inorg. Chem., 1972, 11, 1441. 57
  - G. Busca, L. Marchetti, G. Centi and F. Trifirò, J. Chem. Soc., 58 Faraday Trans. 1, 1985, 81, 1003.
  - 59 G. Busca, G. Centi, L. Marchetti and F. Trifirò, Langmuir, 1986, 2, 568.
  - I. Chen, C. Kikuchi and H. Watanabe, J. Chem. Phys., 1965, 42, 60 186.
  - Ph. de Montgolfier, P. Meriaudeau, Y. Boudeville and M. Che, 61 Phys. Rev. B, 1976, 154, 1788.
  - H. A. Weakliem and D. S. McClure, J. Appl. Phys., 1962, 33, 347. 62
  - H. Demiryout, K. E. Nietering, R. Surowiec, S. I. Brown and D. 63 R. Platts, Appl. Opt., 1987, 26, 3803.
  - R. G. Herman, K. Klier, G. W. Simmons, B. P. Finn, J. B. Bulko and T. P. Kobylinski, J. Catal., 1979, 56, 407.
  - 65 E. Caruthers, L. Kleimmann and H. I. Zhang, Phys. Rev. B, 1973, 7, 3753.
  - 66 D. J. Hucknall, Selective Oxidation of Hydrocarbons, Academic Press, London, 1974.
  - 67 B. M. Reddy, in Catalytic Selective Oxidation, ed. S. T. Oyama and J. W. Hightower, ACS Symp. Ser. 523, ACS, Washington, 1993, p. 204.
  - 68 F. Cavani, G. Centi, E. Foresti, F. Trifirò and G. Busca, J. Chem. Soc., Faraday Trans. 1, 1988, 84, 237.
  - F. Cavani and A. Riva, US Pat. 4870195, 1989, assigned to Alu-69 suisse Italia SpA.
  - R. Nyholn and N. Martenson, Solid State Commun., 1981, 40, 70 311.
  - C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder and J. E. 71 Muileuberg, Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics Div., Perkin Elmer Co., 1979.

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