# Effect of potassium addition to the $TiO_2$ support on the structure of $V_2O_5/TiO_2$ and its catalytic properties in the oxidative dehydrogenation of propane

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Vanadium oxide has been deposited by a grafting technique onto  $TiO_2$  anatase, both pure and doped with potassium [(1.2 and 2.5) atoms nm<sup>-2</sup>]. The V content varied between 0.1 and 20 atoms nm<sup>-2</sup> [0.01–2 V<sub>2</sub>O<sub>5</sub> monolayers (ML)]. The prepared samples were characterized by X-ray photoelectron spectroscopy (XPS), <sup>51</sup>V magic-angle spinning (MAS) NMR and a surface potential (SP) technique and tested as catalysts in the oxidative dehydrogenation (ODH) of propane and propan-2-ol decomposition, a probe reaction for acid-base properties. From the XPS and SP data it has been inferred that VO<sub>x</sub> are located beside the K centres on the bare surface of TiO<sub>2</sub> with the lower K content sample, whereas they cover the K-doped fraction of the surface for the sample with higher K content. Monomeric and polymeric VO<sub>x</sub> species and V<sub>2</sub>O<sub>5</sub> were detected by <sup>51</sup>V NMR on pure and K-doped catalysts. For the K-doped samples the polymeric species were observed only at high V content and new tetrahedral VO<sub>x</sub> species and traces of KVO<sub>3</sub> appeared. It has been found that the presence of K on the TiO<sub>2</sub> surface leads to (*a*) a decrease in the reducibility of the vanadia phase at low V content; (*b*) a decrease in the surface potential (electronic work function); (*c*) a decrease in acidity and increase in basicity and (*d*) a decrease in the total activity for ODH of propane. The pattern of the activity and selectivity is observed at a vanadium content corresponding to *ca.* 40% of a V<sub>2</sub>O<sub>5</sub> ML. At higher K content, higher amounts of vanadium (>1 ML) are required to obtain the same catalytic performance. Polymeric [VO<sub>x</sub>] species seem to be more active and selective in the ODH of propane than monomeric species or bulk V<sub>2</sub>O<sub>5</sub>.

Several papers have been published concerning the effect of potassium, present as an impurity in commercial TiO<sub>2</sub> supports or added intentionally to  $V_2O_5/TiO_2$  catalysts, on their structure and physicochemical and catalytic properties in some oxidation reactions. The structural studies have shown possible formation of potassium vanadates, vanadium-potassium bronze or potassium titanates<sup>1,2</sup> and modification of the vanadium-oxygen bond energy.<sup>3-7</sup> A decrease in acidity<sup>3,7-9</sup> and increase in basicity<sup>9-11</sup> have also been reported. These effects are particularly evident at high K/V ratio. It has also been suggested that potassium may influence the strength of the bond between the vanadia species and the TiO<sub>2</sub> support.<sup>5</sup> No information is, however, available about the mutual distribution of different vanadium and potassium species on the TiO<sub>2</sub> surface.

The oxidation reactions studied on K-doped  $V_2O_5/TiO_2$  catalysts include the oxidation of *o*-xylene,<sup>3,8,12</sup> toluene,<sup>2,12</sup> butadiene,<sup>4</sup> methanol<sup>5</sup> and, most recently, the ODH of propane.<sup>9-11</sup> This latter reaction is of great interest because of its potential application as a source of cheap propene. The presence of potassium in the vanadia/titania catalyst generally decreased the total activity. Its effect on yield and/or selectivity to partial oxidation products was positive or negative depending on the oxidized molecule, on the vanadium and potassium contents and on the reaction conditions.

For the ODH of propane, it has been shown that introduction of potassium after, or simultaneously with, the deposition of the vanadia phase onto the titania anatase support leads to an increase in selectivity to propene.<sup>9-11</sup> The Kpromoted  $V_2O_5/TiO_2$  oxides appeared to be quite promising catalysts for this reaction, the maximum yield of propene amounting to *ca.* 10%. The catalysts studied in ref. 9–11 contained high amounts of the vanadia phase [5 (theoretical) ML in most cases, where 1 ML corresponds to 10 V atoms nm<sup>-2</sup>,<sup>13</sup>] the K/V ratio being fixed at 0.1. No studies have been performed so far with a low (submonolayer) content of vanadia, where the support effect is usually most evident. Similarly, no information is available on the effect of potassium, present on the TiO<sub>2</sub> surface (*e.g.* as an impurity) before deposition of vanadia, on the catalytic performance of  $V_2O_5/TiO_2$  catalysts in the ODH of propane.

In our earlier work, on the effect of potassium introduced in a controlled way onto the TiO<sub>2</sub>surface,<sup>14</sup> 1 ML of K was estimated to contain 2.5 atoms nm<sup>-2</sup>.

In the present work the catalysts prepared by deposition of small amounts of vanadia (below or slightly above one vanadia ML) on a titania surface doped with 1.2 and 2.5 atoms  $nm^{-2}$  (0.5 and 1 ML) have been characterized and tested in the ODH of propane. <sup>51</sup>V NMR, XPS and SP techniques were applied in an attempt to detect different VO<sub>x</sub> and KVO<sub>x</sub> species, their mutual distribution on the titania surface and the effect of doping of the TiO<sub>2</sub> support with K on the catalytic properties of  $V_2O_5/K + TiO_2$  catalysts. The acidbase properties of the catalysts have been also tested using the propan-2-ol decomposition probe reaction. It has been shown previously that the rate of propan-2-ol dehydration to propene is a measure of the catalyst acidity, whereas the ratio of acetone (from dehydrogenation) to propene can be correlated with the basicity.<sup>15</sup>

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### **Preparation of catalysts**

Three series of vanadia/titania samples were prepared using, as a support, pure  $\text{TiO}_2$  (series I),  $\text{TiO}_2$  containing K on the surface: 1.2 atoms nm<sup>-2</sup> (series II) and 2.5 atoms nm<sup>-2</sup> (series III). The V content varied between 0.8 and 20 atoms nm<sup>-2</sup>, which corresponded to 0.08 and 2 (theoretical) ML of vanadia phase.

The samples are denoted in the text by symbols xK Ti yV, where x is the number of K atoms nm<sup>-2</sup> on the TiO<sub>2</sub> surface and y is the number of V atoms nm<sup>-2</sup>. The titania support was a commercial product from Tioxide (BET area 27 m<sup>2</sup> g<sup>-1</sup>), calcined before use for 4 h at 700 °C. Its BET area after calcination was 23 m<sup>2</sup> g<sup>-1</sup>. XRD analysis confirmed it to be pure anatase, no surface impurities were detected by XPS analysis, elementary analysis with a plasma torch (ICP-AES) showed, however, the presence of Cr (12 ppm), Cu (160 ppm) and S (0.13 wt.%). After calcination at 700 °C no sulfur was detected in the support.

Potassium was introduced onto the  $TiO_2$  surface by impregnation from a KHCO<sub>3</sub> solution, evaporation, drying for 12 h at 120 °C and calcination for 4 h at 500 °C.

Vanadium was deposited on the supports by the grafting technique in anaerobic conditions, using vanadyl isopropoxide dissolved in toluene as a precursor. The appropriate amounts of isopropoxide solution were introduced, under continuous stirring, to a vessel containing a suspension of the support in toluene and stirred for 10 min. Toluene was then removed by evaporation at 40 °C and the remaining yellow powder was dried for 12 h at 100 °C and calcined in dry air for 4 h at 400 °C.

## Techniques

NMR measurements. <sup>51</sup>V MAS NMR spectra were recorded at 105.2 MHz on a Bruker ASX 400 spectrometer equipped with an MAS probe for 4 mm od rotors. Spinning speeds up to 15 kHz were used. In all experiments, a single pulsed excitation was applied with a pulse width of 1  $\mu$ s ( $\pi/12$  flip angle) and recycling time of 0.7 s. The isotropic chemical shifts were referred to external VOCl<sub>3</sub> and were not corrected for second-order quadrupolar induced shifts. V<sub>2</sub>O<sub>5</sub> was used as a second external reference ( $\delta_{iso} = -609$  ppm). The  $\delta$  scale is positive towards lower shielding.

Surface potential. This was measured by the vibrating condenser method; the method and the experimental set-up have been described in ref. 14. The measurements were performed under a flow of 20% O<sub>2</sub> in Ar in the temperature range 50– 450 °C. The values of the surface potential,  $\Phi$ , reported in the text are relative to the graphite electrode, an increase in  $\Phi$ indicating that the surface becomes more negatively charged. The surface potential values were reproducible within 5 mV for a given sample.

**XPS spectra.** These were recorded with an AEI-ES 200B spectrometer. The atomic ratio of the elements on the surface,  $n_A/n_B$ , was calculated from the intensity ratio  $I_A/I_B$  with the formula:  $I_A/I_B = \sigma A/\sigma B$ .  $(E_A^{kin}/E_B^{kin})^{1.77}$ .  $n_A/n_B$ ; values of  $\sigma$  being taken from ref. 16.

Catalytic activity measurements. The activity of the catalysts in ODH of propane was measured in a fixed bed flow apparatus in the temperature range 300-450 °C. The reaction mixture contained 5 vol.%  $C_3H_8$  and 15 vol.%  $O_2$  diluted in nitrogen. 1 ml aliquots of the samples were used in the experiments, the contact time being 1 s. Analysis of products and unreacted propane was performed with on-line chromatography. Propene, carbon monoxide and carbon dioxide were found to be the main reaction products, the amount of  $C_2$  hydrocarbons and the oxygenates (acrolein, acetaldehyde, acrylic and acetic acid) were below 1% of the total amount of products.

**Decomposition of propan-2-ol.** The decomposition to propene and acetone was studied at 170 °C with the pulse method, using dried helium as a carrier gas. 0.1 g of the sample and 2  $\mu$ l of propan-2-ol were used and the total flow rate of helium was 30 ml min<sup>-1</sup>. Prior to the test, the samples were treated in a stream of dried helium for 2 h at 250 °C. Gas chromatographic analysis of the products was performed. The conversion of propan-2-ol decreased slightly with the successive pulses, owing to formation of a carbon deposit, the propene yield per pulse decreased faster than that of acetone. The amounts of products per pulse reported later pertain to the first pulse *i.e.* to fresh catalysts.

# **Results and Discussion**

### **XPS** measurements

Table 1 lists the binding energies  $(E_b)$  of different elements in the three series of catalysts, the Ti  $2p_{3/2}$  signal with  $E_b = 459$ eV being taken as a reference. The values of  $E_{\rm b}$  for the O 1s level are practically constant, those of V  $2p_{3/2}$  are constant for most of the samples,  $517 \pm 0.2$  eV, the value typical of the  $V^{5+}$  ions. Lower (by ca. of 0.6 eV) values, observed for the samples with low V content in series I, indicate partial reduction of  $V^{5+}$  ions to lower oxidation states. Partial reduction of the vanadia phase present in a monolayer structure in  $V_2O_5/TiO_2$  catalysts has been previously evidenced by EPR<sup>17</sup> and chemical analysis.<sup>17,18</sup> Vanadium deposited on Kpromoted TiO<sub>2</sub> (series II and III) is, on the other hand, present as V<sup>5+</sup>, irrespective of the V content. This implies that the presence of potassium hinders the reduction of vanadium. The  $E_b$  values for the K 2p level decrease with the V content, suggesting some loss of the cationic character of potassium. Note that the potassium  $E_b$  values for the V-Ti-K-O samples studied here are higher than those of potassium vanadate and potassium-vanadia bronze,  $E_b = 292.6$  eV has been recorded for KVO<sub>3</sub>, KV<sub>3</sub>O<sub>8</sub> and K<sub>3</sub>V<sub>5</sub>O<sub>14</sub> prepared as reference com-pounds, and  $E_b = 292.0$  eV for K<sub>0.51</sub>V<sub>2</sub>O<sub>5</sub> bronze, O 1s at 530 eV being taken as a reference.

**Table 1** Binding energies,  $E_b$  of different elements in the series Ti yV, 1.2K Ti yV and 2.5K Ti yV

	$E_{b}/eV$					
sample	Ti 2p <sub>3/2</sub>	O 1s	V 2p <sub>1/2</sub>	V 2p <sub>3/2</sub>	K 2p <sub>3/2</sub>	
series Ti yV						
Ti 1.2V	459	530.1	524.1	516.3	_	
Ti 2.4V	459	530.3	524.2	516.4	_	
Ti 4.8V	459	530.4	524.5	517.0		
Ti 7V	459	530.2	524.5	517.0		
<b>Ti 10V</b>	459	530.2	524.4	517.0	_	
Ti 12V	459	530.1	524.6	516.9	_	
Ti 20V	459	530.2	524.5	517.1	_	
series 1.2K Ti yV						
1.2K Ti 0.8V	459	530.2	524.6	516.8	293.9	
1.2K Ti 1.2V	459	530.1	524.3	516.7	294.0	
1.2K Ti 2.4V	459	530.2	524.4	516.8	293.6	
1.2K Ti 3.6V	459	530.2	524.5	516.9	293.6	
1.2K Ti 7V	459	530.1	524.5	516.9	293.4	
1.2K Ti 10V	459	530.2	524.5	516.8	293.2	
series 2.5K Ti yV						
2.5K Ti 3.6V	459	530.1	524.5	516.9	293.5	
2.5K Ti 10V	459	530.0	524.4	516.9	293.4	
2.5K Ti 20V	459	530.6	524.7	517.5	293.2	



Fig. 1 Variation of the surface atomic ratio nV/nTi with total V content for undoped and K-doped catalysts: (×) Ti yV, ( $\bigcirc$ ) 1.2K Ti yV and ( $\blacklozenge$ ) 2.5K Ti yV series

Figure 1 shows the variation in the surface atomic ratio V: Ti with the total V content. For the three series, the ratio increases at low V content to a constant value reached at ca. 10 atoms  $nm^{-2}$ . Similar variation in the V/Ti ratio has been observed previously for V2O5/TiO2 catalysts prepared by other methods.<sup>19,20</sup> It has been ascribed to the gradual covering of the TiO<sub>2</sub> surface with a two-dimensional layer of vanadia phase, followed by formation of 'towers' of crystalline  $V_2O_5$  at a V content higher than one theoretical ML. The presence of potassium on the support surface does not change the V/Ti ratio significantly at low V content. A small increase in V/Ti ratio can, however, be observed for the Ti series doped with 2.5 K atoms nm<sup>-2</sup> at higher V content, which suggests better dispersion of the vanadia phase in this case. A similar effect of potassium has been reported for V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> samples with higher V content, where potassium was introduced after deposition of vanadia on the titania support.<sup>9</sup> Fig. 2 shows the V/K ratio and the intensities of the K signal (area of the K 2p peak normalized to the O 1s peak) as a function of the total V content for the K-doped series of catalysts. For the 1.2 K atoms nm<sup>-2</sup> series, the intensity of the potassium peak does



**Fig. 2** Variation of the surface atomic ratio nV/nK (empty symbols) and the intensity of the K 2p signal (filled symbols) with total V content for K-doped catalysts: ( $\bigcirc \bullet$ ) 1.2K TiyV series, ( $\diamondsuit \bullet$ ) 2.5K Ti yV series

not change with the V content, suggesting that vanadiumcontaining species are located beside potassium atoms on the fraction of the TiO<sub>2</sub> surface not covered with potassium. For the 2.5 K atoms  $nm^{-2}$  series, the potassium intensity decreases, beginning from the samples with V content of 3.6 V atoms  $nm^{-2}$ . This implies that, in this case, vanadium species partially cover the K-promoted surface of the titania support. Some fraction of potassium atoms is still exposed on the surface, even at high vanadium content.

# NMR data

<sup>51</sup>V MAS NMR spectra of some catalysts from the series Ti yV are shown in Fig. 3. At low V content, 2.4 and 3.6 atoms nm<sup>-2</sup>, two species are present: species 1 characterized by  $\delta_{iso} = -639$  ppm and species 2 with  $\delta_{iso} = -550$  ppm. These two vanadium species exhibit nearly the same sideband pattern and their chemical shift anisotropy (CSA) is clearly higher than for tetrahedral species observed in V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts<sup>21-25</sup> and in vanadium-based compounds.<sup>26-29</sup> The similar spectroscopic characteristics of the two signals are consistent with surface vanadium species in a distorted polyhedron environment. Accurate values for CSA and quadrupolar parameters can be obtained by simulation of experimental spectra:<sup>30</sup> further discussion of these NMR parameters will be the subject of a separate paper.<sup>31</sup> The absence of tetrahedral species in the present samples can be due to the different



Fig. 3  $^{51}$ V MAS NMR spectra of samples Ti yV (isotropic lines are indicated by filled arrows)

method of preparation and the different  $\text{TiO}_2$  support and the fact that the NMR spectra were recorded in ambient conditions. Comparison of our results with those of Eckert and coworkers<sup>22,24</sup> shows that the signals corresponding to species 1, 2 and the  $V_2O_5$ -like species (recorded by us with a high-speed MAS technique) can be present in the envelope of broader, low-resolution spectra published by these authors. We do not observe, on our catalysts, the signal at -660 ppm, detected by them with a wide-line NMR technique for dehydrated samples, or samples with sulfate, phosphorus and potassium impurities, and assigned to tetrahedral monomeric species. This difference may be due to the fact that our NMR spectra were recorded under ambient conditions in which V assumes octahedral coordination.

The amount of species 2 increases with the V coverage (2.4– 3.6 atoms while the amount of species 1 remains nearly constant. For the highest V loading (10 atoms nm<sup>-2</sup>), the <sup>51</sup>V MAS NMR spectrum is highly modified. This large modification corresponds to the formation of V<sub>2</sub>O<sub>5</sub> characterized by  $\delta_{iso} = -609$  ppm. V<sub>2</sub>O<sub>5</sub> is predominant at this V content, species 2 at *ca.* -550 ppm are, however, always present. Moreover, one cannot exclude the presence of species 1 which can be also observed at the bottom of the different sidebands of V<sub>2</sub>O<sub>5</sub>.

The 51V NMR results can be discussed in the light of the literature data. Vanadium (v) in species 1 appears to be more shielded than in  $V_2O_5$  and in species 2 (Table 2). We can assume that the magnetic shielding of vanadium is directly affected by the electron density around oxygen atoms which depends on the electronegativity, X, of the second neighbouring metal atom in the second coordination sphere. Recent <sup>51</sup>V NMR studies on different metavanadates<sup>25,27</sup> and on  $V_2O_5$  $Nb_2O_5$  catalysts<sup>32</sup> have shown that the values of isotropic chemical shifts of vanadium move toward more negative values as the electronegativity of the second metal atom decreases. Consequently, the higher electron density around vanadium in species 1 can be attributed to its stronger interaction with TiO<sub>2</sub> than in species 2 (X of Ti is lower than X of V). This result is in agreement with the XPS data (Table 1) which indicate a slight reduction of  $V^{5+}$  (lower  $E_b$  of V) at low V content. Raman spectroscopic studies<sup>7,33</sup> have shown the presence of monomeric VO<sub>x</sub> species at the lowest V content and polyvanadates at higher V content. In keeping with the Raman studies, 33, 34 it can be suggested that species 1 are monomeric  $VO_x$  species with a V coordination number greater than four, interacting strongly with the support.

Since vanadium in species 2 is less shielded than in species 1, species 2 seems to be in a weaker interaction with  $TiO_2$ . On the other hand, V—O bond lengths and also V—O—V bond angles, in addition to the electronegativity of the second neighbouring atom, are significant parameters which can affect the <sup>51</sup>V shielding.<sup>27,28</sup> Species 2 can be identified as a polymeric species in which the vanadium has the same geometrical environment as in species 1, but different V—O bond lengths and/or V—O'—V angles.<sup>31</sup> The identification is supported by the fact that the amount of species 2 increases with V loading until ML coverage is attained, in agreement with

**Table 2** <sup>51</sup>MAS NMR analysis:  $\delta$  iso values for vanadium species of different samples

sample	(1) /ppm	(2) /ppm	(3) /ppm	(4) /ppm	V <sub>2</sub> O <sub>5</sub> ppm
Ti 2.4V	-636	-557			
Ti 3.6V	-639	- 559	_	_	
Ti 10V	-639	- 560			- 609
1.2K Ti 3.6V	-615	- 546	- 528		
2.5K Ti 3.6V	-602		-532	- 554	
2.5K Ti 10V		- 560	- 532	—	-609

the increase in the content of polymeric vanadates observed in the Raman studies of Went *et al.*<sup>33</sup> At the highest V loading (10 V atoms nm<sup>-2</sup>), crystallites of V<sub>2</sub>O<sub>5</sub> appear but species 2 are always present, the V<sub>2</sub>O<sub>5</sub>/species 2 ratio being *ca.* 5.

Fig. 4 displays the <sup>51</sup>V MAS NMR spectra of the xK Ti 3.6V samples. The general trend observed, when compared with the non-doped samples, is a downfield shift of signals, which indicates that the electron density around the vanadium atom decreases when potassium is present, particularly for species 1. In the 1.2K Ti 3.6V sample, the shift is +24 ppm for species 1 and +13 ppm for species 2, however, the shape of the sideband pattern is not altered. The lowering of the electron density around  $V^{5+}$  ions seems to be in contrast to the conclusion of Busca et al.,6,7 who deduce from their IR data that the electron density around V atoms in vanadyl groups increases in the presence of potassium. This discrepancy can be tentatively explained if we recall that (as stated by Busca et al.), different vanadyl species may exist on the  $TiO_2$  surface. Potassium introduced onto our samples before the deposition of the vanadia phase may block the centres of the anchoring of those vanadyl groups which are in strong interaction with the support, favouring the formation of more acidic V-O groups. Such groups were observed by Busca et al. at higher vanadia content on the undoped samples.6,7

The lower values of the isotropic chemical shift observed by species in our NMR studies would reflect, rather, the forma-



Fig. 4 <sup>51</sup>V MAS NMR spectra of the xK Ti 3.6V samples

tion of these types of vanadyl, with a small decrease in the electron density around the  $V^{5+}$  ions.

In the case of the 2.5K sample, there is a major modification in the shape of the spectrum: two signals appear, at -532 and -552 ppm. The small but very sharp signal at -552 ppm can be attributed to KVO<sub>3</sub>-like species.<sup>29</sup> The isotropic peak at -532 ppm is associated with a sideband pattern very different from that observed in the absence of potassium. The shape of this NMR signal allows a rough estimation of the chemical shift anisotropy: 300 ppm. It could be assumed that a new species 3, nearly symmetric and probably four-fold coordinated, is responsible for this NMR signal (this species was also detected in small quantities on 1.2K Ti 3, 6V). Furthermore, it is important to note that species 1 are always present with a downfield shift of +37 ppm (the shift increasing with the K content) but species 2 are not observed. When the K monolayer coverage is reached, there are only monomeric species 1 in weaker interaction with TiO<sub>2</sub> than in the absence of K, tetrahedral species 3 and a small quantity of KVO<sub>3</sub>.

<sup>51</sup>V MAS NMR spectra of Ti 10V and 2.5K Ti 10V are presented in Fig. 5. At this vanadium coverage, the predominant species is  $V_2O_5$ . In the presence of K, species 2 seems to be always present but the width of the signal at -560 ppm does not allow an accurate determination of the isotropic peak for these species. However, a very small peak at  $\delta = -530$  ppm can be assigned to tetrahedral species 3.

In summary, at low V content the introduction of potassium onto the  $TiO_2$  anatase before the deposition of vanadium leads to a downfield shift of species 1 and 2. For the K monolayer coverage (2.5K samples), species 2 disappear and the formation of more symmetric vanadium species



Fig. 5  ${}^{51}$ V MAS NMR spectra of the xK Ti 10V samples

(tetrahedral and  $KVO_3$ ) can be explained by a weakening of the interaction between vanadium and the support. It appears, moreover, that a higher V content is necessary for formation of polymeric oxovanadium species (2) when K monolayer coverage is reached (for the 2.5K Ti 10V sample).

### Surface potential, $\Phi$

Fig. 6 presents the changes in the surface potential,  $\Phi$ , with temperature for the samples of the Ti vV series. Over the whole range of temperature studied, the  $\Phi$  values are higher for vanadium containing preparations than for pure  $TiO_2$  and depend on the V content. For pure  $TiO_2$ , the  $\Phi$  values increase significantly with temperature, indicating an increase in the negative charge on the surface. Such an increase can be ascribed to transformation of the chemisorbed oxygen species to more negatively charged forms, *e.g.*  $O_2 + e^- \rightarrow O_2^-$  or  $O^- + e^- \rightarrow O^{2-}$ ;<sup>35,36</sup> it can also be due to an increase in the amount of chemisorbed oxygen with temperature. The changes in  $\Phi$  with temperature decrease with increasing V content: for the samples containing 7-10 atoms nm<sup>-2</sup> the  $\Phi$ values are practically constant between 90 and 450 °C. This suggests that the centres of the oxygen sorption and/or transformation of different oxygen species, present on the TiO<sub>2</sub> surface are gradually covered by the deposited VO<sub>x</sub> groups, the dispersed vanadia phase having different sorptive properties than the TiO<sub>2</sub> support. Previous studies have shown that the surface potential in air of V<sub>2</sub>O<sub>5</sub>, pure or dispersed on the anatase surface in quantities equal or exceeding a theoretical monolayer, is within ca. 20 mV, constant over the temperature range 100-450 °C.<sup>9,36</sup> Figure 7 shows the analogous curves for K-doped samples of the 1.2K Ti yV and 2.5K Ti yV series. Doping of the TiO<sub>2</sub> support with K leads to a decrease in  $\Phi$ and to a levelling off of the  $\Phi$  values at different temperatures; the effect being more pronounced for the samples with higher K content. Deposition of V on K-doped TiO<sub>2</sub> leads to an increase in  $\Phi$ , the  $\Phi$  values for both series II and III being, however, much lower (by ca. 1 V) than those for the K-free samples. The smaller  $\Phi$  values indicate that the energy barrier for electron transfer from the catalysts to adsorbed molecules is lowered in the presence of potassium. The reoxidation step in the redox cycle of the oxidation reactions: O2  $+ 4e^- \rightarrow 2O^{2-}$  should then be easier for K-doped catalysts.

In Fig. 8 the values of  $\Phi$  at 450 °C are plotted as a function of the V content for the series of undoped and K-doped Ti V



**Fig. 6** Changes in the surface potential,  $\Phi$ , with the temperature for undoped catalysts: series I: Ti yV. ( $\Box$ ) 0, ( $\blacklozenge$ ) 1.2, ( $\triangle$ ) 3.6, ( $\blacksquare$ ), 7 and ( $\bigcirc$ ) 10 atoms nm<sup>-2</sup>.



Fig. 7 Changes in the surface potential,  $\Phi$ , with temperature for K-doped catalysts: (a) series II: 1.2K Ti yV (b) series III: 2.5K Ti yV. ( $\Box$ ) 0, (\*) 1.8, ( $\Delta$ ) 3.6, ( $\bigcirc$ ) 10 and ( $\diamondsuit$ ) 20 atoms nm<sup>-2</sup>.



**Fig. 8** Values of  $\Phi$  at 450 °C as a function of V content: (x) Ti yV, (O) 1.2K Ti yV and ( $\blacklozenge$ ) 2.5K Ti yV series

samples. Since, at this temperature, the electronegative, mobile  $O_2^-$  and  $O^-$  species are not observed on the surface of oxides,<sup>37</sup> the surface potential in the oxygen atmosphere reflects the dipole structure of the uppermost, fully oxidized layer of the oxide. The polarized surface Me $-O_x$  groups with oxygen atom oriented towards the exterior of the solid give rise to a surface negative charge, whereas those with exposed Me cations lead to a positive charge: the value of  $\Phi$  would depend on the relative amounts of the two types of surface dipoles ( $\delta^-$ ) O-Me and ( $\delta^+$ ) Me-O, on the dipole strength and their orientation with respect to the surface.

The surface potential for undoped Ti–V samples [Fig. 8] increases linearly with the V content up to *ca.* 3.6 atoms  $nm^{-2}$ , and then decreases to a constant value at *ca.* 10 atoms  $nm^{-2}$ . This pattern of change in  $\Phi$  can be interpreted by assuming that different VO<sub>x</sub> species are present on the TiO<sub>2</sub> surface for different amounts of deposited vanadia phase; each of these species is, moreover, characterized by a different surface potential owing to the different dipole structure.

The linear increase in  $\Phi$  at low vanadium content [ca. 100 mV (V atom)<sup>-1</sup>] indicates that the TiO<sub>2</sub> surface is covered gradually by  $\overline{VO}_x$  species more negatively charged than the support surface. The decrease in  $\Phi$  at higher V content suggests the appearance of new species, less negatively charged than the first ones. From a V content corresponding to one theoretical monolayer of vanadia the surface potential attains a constant value, implying that the type of the dispersed species does not change at higher V content. As discussed in the preceding paragraph the literature data and the <sup>51</sup>V NMR data of this study show the presence of monomeric, isolated  $VO_x$  species and chains of polyvanadates V-O-V-O at lower V content, and bulk  $V_2O_5$  at V concentrations close to monolayer coverage. The XPS data of this study indicate, moreover, that agglomeration of vanadium (most probably in the form of  $V_2O_5$ ) is observed for the studied catalysts well below 10 atoms nm<sup>-2</sup>

It seems evident that the monomeric and polymeric species with an oxygen atom sticking out of the surface would contribute more to the negative charge on the surface (resulting in higher  $\Phi$  values), than V<sub>2</sub>O<sub>5</sub> crystals on faces where both V and O atoms are exposed. This could account for the observed pattern of changes in  $\Phi$  with the V content. With K-doped TiO<sub>2</sub> the increase in  $\Phi$  to a constant value has only been observed when vanadium is introduced (Fig. 8).

The shape of the curves is, moreover, different for the series with different K content, the constant value of  $\Phi$  being reached at *ca.* 3.6 atoms nm<sup>-2</sup> and 15 atoms nm<sup>-2</sup> for the 1.2K and 2.5K series, respectively. The  $\Phi$  values at high V content are, however, practically the same for both series and significantly lower than those for the undoped samples. The latter fact suggests that some fraction of the K-doped support surface is still exposed, even at greater than monolayer coverage.

In the region of the linear increase in  $\Phi$  with the V content, the  $\Phi$  value can be represented by a simple equation:

$$\Phi_{\rm M} = \Phi_{\rm TiO_2} + \alpha_{\rm K} N_{\rm K} + \alpha_{\rm V} N_{\rm V} \tag{1}$$

where  $\alpha_{\mathbf{K}}$  and  $\alpha_{\mathbf{V}}$  are coefficients which represent the changes in  $\Phi$  per atom of potassium or vanadium,  $N_{\mathbf{K}}$  and  $N_{\mathbf{V}}$  are the numbers of K and V atoms.

The value of  $\alpha_{\rm K}$  obtained from ref. 14 amounts to -670 mV (K atom)<sup>-1</sup>, the value of  $\alpha_{\rm V}$  calculated from the linear part of curve (a) is 100 mV and from curve (b), 86 mV.

Table 3 gives the values of  $N_{\rm K}$  calculated from eqn. (1) for different amounts of  $N_{\rm V}$  deposited on 1.2K and 2.5K TiO<sub>2</sub> supports and for the two values of  $\alpha_{\rm V}$ . As seen, the number of K atoms exposed on the surface of 1.2K Ti yV series, calculated from eqn. (1) is close to that introduced on the support surface. This implies that vanadium is located on the fraction

**Table 3** Numbers of atoms  $N_{\rm K}$  and  $N_{\rm V}$  calculated from surface potential data

	$N/\text{atoms nm}^{-2}$				
	introduced		calculated <sup>a</sup>		
support	v	K	$\overline{\mathbf{K}(a)}$	K(b)	
	1	1.2	1.23	1.23	
1.2K Ti	2.4	1.2	1.29	1.24	
	3.6	1.2	1.35	1.28	
2.5K Ti	3.6	2.5	2.19	2.11	

<sup>a</sup> Assuming  $\alpha_{\rm K} = -670$  mV and  $\alpha_{\rm V} = 100$  mV (a) or  $\alpha_{\rm V} = 86$  mV (b) in eqn. (1).

of bare TiO<sub>2</sub> surface not covered with potassium. In contrast,  $N_{\rm K}$  calculated for the 2.5K Ti 3.6V sample is lower (by *ca.* 0.4) than that corresponding to the 2.5K TiO<sub>2</sub> support, which suggests that the deposited vanadia phase partly covers the K centres on the TiO<sub>2</sub> surface. The mutual distribution of vanadium and potassium on the titania surface is supported by the XPS results discussed earlier.

# **Catalytic activity**

Fig. 9 gives the values of total conversion of propane, selectivity to propene and the CO/CO<sub>2</sub> ratio at different reaction temperatures for the three series of catalysts. For the K-free Ti yV series, the conversion increases and the selectivity to propene decreases with increase in the vanadium content. At lower temperatures, 350 and 400 °C the increase in the propane conversion is linear up to  $3.6V \text{ nm}^{-2}$  and levels off for the Ti 10V sample, the conversion values per V atom  $nm^{-2}$  being equal to ca. 11 for Ti 2.4V and Ti 3.6V samples and only 6.8 for the Ti 10V one. This result implies that not all the vanadium is accessible to the reacting molecules in the case of Ti 10V sample, suggesting a certain degree of agglomeration of vanadia phase by formation of three-dimensional V2O5-like species, already at one monolayer coverage. Alternatively, one could propose the formation of  $V_x O_y$  species of different catalytic activity in the vanadium content range between 3.6 and 10 V nm<sup>-2</sup>. In view of the XPS data which show levelling off of the the surface V/Ti ratio already at a vanadium content of 7 V nm<sup>-2</sup>, agglomeration of the vanadia on the surface appears to be the more likely explanation.

The K-doped samples show, on the whole, lower conversions of  $C_3H_8$ , higher selectivities to propene and lower values of the CO/CO<sub>2</sub> ratio, as compared with the K-free series. This effect was previously observed for the vanadia/ titania catalysts of higher vanadium content, in which potassium was introduced after, or simultaneously with, the deposition of vanadia phase on the titania support.<sup>9-11</sup>

Some differences between the catalysts in the 1.2K and 2.5K series can, however, be observed. With the 1.2K Ti yV samples, the conversion increases with the vanadium content up to 3.6 atoms nm<sup>-2</sup> and slightly decreases (at 400 °C) or remains practically constant (at 450 °C) at higher concentrations of vanadium (7 and 10 atoms nm<sup>-2</sup>). The selectivity to propene follows the changes in the conversion, a maximum in selectivity being observed at 3.6 atoms nm<sup>-2</sup>.

With the 2.5K Ti yV samples the conversion increases in the vanadium content range 3.6-20 atoms  $nm^{-2}$ . This is accompanied by an increase in selectivity to propene at reaction temperatures of 350 and 400 °C and a slight decrease with increasing vanadium content at 450 °C.

At low vanadium content, 3.6 atoms  $nm^{-2}$ , the catalyst prepared on 1.2K titania is more active and selective than that containing the 2.5K support. At 10 atoms  $nm^{-2}$  the values of the conversion and selectivity to propene for the 1.2K Ti 10V preparation are on the other hand very close to those for the 2.5K Ti 10V sample. Recall that the surface V/K ratio determined from the XPS data is lower for 2.5K Ti 3.6V than for 1.2K Ti 3.6V sample, whereas it is very similar for both the 1.2K and 2.5K series with vanadium content 10 atoms nm<sup>-2</sup>.

Similarly, the values of surface potential, which reflect the relative amounts of the two elements on the catalyst surface, are close for the 1.2K and 2.5K samples with vanadium content 10 atoms  $nm^{-2}$ , and much different at lower vanadium concentration. The activity and selectivity in ODH of propane appear then to depend on the relative amounts of vanadium and potassium on the surface.

Explanation of the different catalytic behaviour in terms of different  $VO_x$  species present, as shown by the NMR spectra in different catalysts, is rather complex, since in most cases several species are observed. Some observations, however, can be discussed.

For the K-free samples the well dispersed  $VO_x$  species at low vanadium content seem to be more active than the agglomerated ones. In view of the large variations in conversion with the vanadium content the selectivity of different species cannot, however, be compared. As in many of the selective oxidation reactions, the ODH of propane is a parallel-consecutive reaction,<sup>38</sup> in which the intermediate product (propene) can be further oxidized to  $CO_2$ . Hence, the selectivity to propene decreases with increasing conversion and thus the comparison of different catalyts should be made at propane isoconversion.

For the K-promoted series, however, the selectivityconversion dependence is atypical. The selectivity increases in spite of the increase in conversion (*e.g.* between 0.8 and 3.6 atoms  $nm^{-2}$  for the 1.2K series and from 3.6 to 20 atoms  $nm^{-2}$  for the 2.5K series), or decreases when the conversion slightly decreases or is constant (for catalysts containing 3.6–10 atoms  $nm^{-2}$  for the 1.2K series). Such behaviour implies that different vanadium species, present at different vanadium content exhibit different activity and selectivity. For the 1.2K series, the well dispersed species seem to be more active and selective than agglomerated ones, as in the case of non-doped catalysts.

The increase in selectivity with the V content in the range 0.8-3.6 atoms nm<sup>-2</sup> observed for this series suggests, however, that the close vicinity of these well dispersed species (the formation of VO<sub>x</sub> polymeric chains) is necessary for a selective catalyst. In fact, the NMR data suggest an increase in the concentration of polymeric species in this V-content region. The monomeric species appear less selective than polymeric ones. The practically constant value of conversion a V content higher than 3.6 atoms nm<sup>-2</sup> suggests again that agglomerated  $V_2O_5$  is not active in the reaction. Its presence, however, lowers the selectivity. This can be due to enhanced overoxidation of propene to CO<sub>2</sub> which is known to occur on unsupported vanadia.<sup>9</sup> With the 2.5 K series, the increase in selectivity at higher V content (>3.6 atoms  $nm^{-2}$ ) can be ascribed to the appearance of the polymeric species only at higher V content.

Recall that, as indicated by the NMR measurements, at higher K content the polymeric species were not observed at 3.6 atoms  $nm^{-2}$  but only at 10 atoms  $nm^{-2}$ . No conclusions can be drawn about the contribution of the tetrahedral species, observed only on K-doped samples, to the overall activity and selectivity in ODH of propane.

### **Propan-2-ol decomposition**

Table 4 gives the amounts of propene and acetone per pulse for selected samples of the three series under study with V content below (3.6 atoms nm<sup>-2</sup>) or equal to 1 theoretical ML. The amounts of propene, a measure of the acidity, are lower for the K-doped samples than for the undoped ones. Higher



**Fig. 9** ODH of propane at different temperatures for undoped and K-doped catalysts: (a) Ti yV, (b) 1.2K Ti yV, (c) 2.5K Ti yV. ( $\Box$ ) conversion of C<sub>3</sub>H<sub>8</sub>, (**B**) conversion/atoms nm<sup>-2</sup> (**B**) selectivity to C<sub>3</sub>H<sub>6</sub>, (**D**) CO/CO<sub>2</sub>.

 
 Table 4
 Propan-2-ol decomposition on undoped and K-doped catalysts

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sample	propene/ $10^6$ mol m <sup>-2</sup>	acetone/ $10^6$ mol m <sup>-2</sup>	
Ti 3.6V	0.53	2.1	
1.2K Ti 3.6V	0.03	2.0	
2.5K Ti 3.6V	0.01	0.9	
Ti 10V	0.86	2.1	
1.2K Ti 10V	0.17	2.3	
2.5K Ti 10V	0.17	2.4	

amounts of propene with the 10 V catalysts can be due to the presence of bulk  $V_2O_5$  detected by NMR: as shown previously<sup>39</sup> crystalline vanadia is much more active in propan-2-ol dehydration than the dispersed monolayer  $VO_x$  species. Both Brønsted and Lewis acidic centres may be involved in dehydration of propan-2-ol to propene.<sup>40</sup> As suggested by the NMR data, vanadium in the vanadyl groups which are formed in the presence of potassium exhibits a small decrease in electron density, which implies higher Lewis acidity. The decrease in the amounts of propene with the K-doped catalysts would then be due rather to the decrease in the concentration of Brønsted sites, by their replacement with potassium ions. The presence of Brønsted acidic sites in  $V_2O_5/TiO_2$  catalysts has been reported by Busca *et al.*.<sup>41</sup>

Dehydrogenation of propan-2-ol to acetone is not much affected by the presence of potassium with the exception of 2.5K Ti 3.6V. It has been shown that, in the  $V_2O_5/TiO_2$ system, acetone is mainly formed on the monolayer species,  $V_2O_5$  being little active in the dehydrogenation.<sup>39</sup> The low dehydrogenating activity of the 2.5 Ti 3.6V catalyst can be related to the absence of  $[VO_x]_n$  polymeric species in this sample, as inferred from the NMR data. At higher V content on 2.5K Ti 10V where the polymeric oxo-vanadium species have been detected, the dehydrogenating properties are, however, restored. The increase in the amount of acetone between 3.6 and 10 (V atoms) nm<sup>-2</sup> for the 2.5K Ti samples can be correlated with the increase in the activity in ODH of propane, reported for the same concentration range in the preceding paragraph. This confirms the role of dehydrogenating centres in determining the activity of the oxydehydrogenating reactions. The results of the propan-2-ol test support, moreover, the hypothesis that it is polymeric  $[VO_r]_n$ groups which are the main active species in dehydro and oxydehydro reactions on vanadia/titania catalysts.

The decrease in the acidity and increase in the basicity (acetone/propene ratio) in the K-doped preparations can account for the modification in catalytic properties in ODH of propane. The elimination of Brønsted acid centres would reduce the non-selective route of oxidation (thus decreasing the total activity) which involves formation of carbocation that is prone to cracking: in the presence of oxygen the cracked fragments can be oxidized to carbon oxides.

On the other hand, the decrease in acidity and increase in basicity would facilitate desorption of propene from K-doped catalysts preventing its overoxidation to  $CO_x$  on the surface, and thus increasing the selectivity to  $C_3H_6$ .

# Conclusion

1. The results presented above allow us to propose a model for the distribution of vanadia species on the surface of K-doped (modified) anatase titania (Fig 10).

The presence of K on the TiO<sub>2</sub>surface does not change the type of main VO<sub>x</sub> species: at low K coverage, as for undoped TiO<sub>2</sub>, monomeric and polymeric vanadia species are recorded at low V content (1 ML  $V_2O_5$ ) and bulk  $V_2O_5$  above 1 ML. At higher K coverage the formation of polymeric species is shifted towards the higher (monolayer) V content: at low V





Fig. 10 Model of distribution of vanadium species on the surface of pure and K-doped titania anatase: (a) Ti yV, (b) 1.2K Ti yV, (c) 2.5K Ti yV. VO<sub>x</sub>: monomeric species (distorted); V-O-V: polymeric species (distorted);  $V'O_x$ : tetrahedral species (symmetric).

coverage mostly monomeric VO<sub>x</sub> species are observed. Additional VO<sub>x</sub> species of tetrahedral symmetry appear on K-doped catalysts. Traces of KVO3 are also recorded at a higher concentration of potassium. The presence of potassium leads to the weakening of the bond between mono or polymeric species and the TiO<sub>2</sub> support.

At K content below 1 ML K (1.2 atoms nm<sup>-2</sup>) the vanadia species are located beside the potassium atoms on the bare fraction of the TiO<sub>2</sub> surface. For a potassium content corresponding to one K ML, the vanadia species cover the K atoms on the support surface also.

2. The presence of potassium on the  $TiO_2$  surface modifies the physicochemical properties of  $V_2O_5/TiO_2$  catalysts, leading to: (a) A decrease in the reducibility of the vanadia species at low vanadium concentration; (b) a decrease in the surface potential (electronic work function) and (c) a decrease in acidity and an increase in the basicity.

3. The activity in the ODH of propane decreases considerably for catalysts prepared on K-doped TiO<sub>2</sub> as compared with the undoped  $TiO_2$  systems.

4. The pattern of activity and selectivity changes with the total V content depends on the amount of K on the support surface: For a K content <1 ML the maximum activity and selectivity is observed at a V content corresponding to ca. 40% of a  $V_2O_5$  ML. At higher K content, higher amounts of V (>1 ML) are required to obtain the same catalytic performance.

5. Polymeric  $[VO_x]$  species seem to be more active and selective in ODH of propane than monomeric species or bulk V<sub>2</sub>O<sub>5</sub>.

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