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## ARTICLE

## Investigation of the elimination of VOC mixtures over a Pd-loaded V-doped TiO<sub>2</sub> support

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The removal of a butanone/toluene mixture over Pd/5%V-TiO<sub>2</sub> and Pd/TiO<sub>2</sub> catalysts has been investigated. The V-doped sample showed a higher performance in the oxidation of butanone and also a butanone/toluene mixture, which was attributed to competition between oxygen species and VOCs on vanadium adsorption sites. However in the presence of both VOCs, Pd/5%V-TiO<sub>2</sub> showed a higher performance than in the elimination of butanone alone. An *operando* DRIFT experiment coupled with a mass spectrometer revealed that both VOCs compete in terms of adsorption at the surface of the catalyst. However, toluene adsorption is decreased by MEK, meaning that the latter oxidizes more easily into its by-products, whose combustion causes variations in the surface temperature of the catalyst, thus enhancing the oxidation of toluene molecules present in the gaseous stream.

### Introduction

The technological advancement of today's society has consequentially led to great developments in industrial processes. However, industrial emissions still pose a great concern in terms of preserving the environment, as volatile organic compounds (VOCs) still constitute a major part of the gases released. Being major contributors to atmospheric pollution and noxious to the environment as well as human health, their presence has urged the scientific community to search for better remediation techniques.<sup>1</sup> Their removal using catalytic oxidation has proven not only to offer more desirable results than thermal combustion but also lower operating temperatures. The advantages of lowering the reaction temperature lie in lowering the energy cost and reducing the formation of by-products sometimes more toxic than their product of origin. Catalytic systems comprising of a supporting material and an active phase provide the above mentioned advantages when used in oxidation reactions. Their efficiency can be modified in order to improve results. This can be achieved by altering the composition or structure of these materials (doping, porosity)<sup>2-5</sup> or loading them with a metallic active phase (such as Pd, Au, Cu, Co etc.)<sup>6-14</sup> capable of

boosting the supported materials activity.

Studies suggested that creating a support with a hierarchical porous frameworks provides larger contact surfaces, which has been linked to a higher activity towards the oxidation of pollutants. Kapoor et al.<sup>15</sup> argued that mesoporous titania provided a better dispersion of Pd and consequently, a better activity towards the decomposition of methanol. Ilieva et al.<sup>16</sup> also proved that a support's mesoporous structure along with the active phase deposition technique played an important role in reducing gold particle size, rendering them more active towards the oxidation of benzene. Doping an oxide catalyst with oxide promoters (Y, V, Nb, Ce etc.) also played an important role in enhancing the catalyst performance. In fact, Labaki et al.<sup>17,18</sup> showed that doping a copper loaded zirconia support with 1% yttrium oxide enhances the catalyst's activity in the oxidation of toluene and propene. Thus, lower oxidation temperatures were achieved. For example, T<sub>50</sub> values (temperature at which 50% conversion of VOC is achieved) dropped from 380 to 250°C for the oxidation of toluene. In fact, the presence of yttrium participates in the formation of CuO particles which are considered to be the most active catalytic sites, therefore a better oxidation rate is achieved at low temperatures. Cavani et al.<sup>19</sup> investigated the effect of promoters (Cs and Sb) on the catalytic activity of a V/Ti/O sample in the oxidation of *o*-xylene. They argued that the promoters ensured a high presence of isolated vanadium, the most active sites in the oxidation of *o*-xylene, whereas in undoped supports, isolated vanadium was obtained only for low amounts of V<sub>2</sub>O<sub>5</sub>. They concluded that the doping process led

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to “a considerable increase of the catalytic activity”. In an earlier published work, we managed to prove the existence of a supplementary interaction between the catalytic support and the active phase loaded onto it.<sup>20</sup> This interaction was provided by the dopants. It consisted of an electron transfer towards the active phase, thus reducing palladium species at room temperature, which consequently reduced  $T_{50}$  values of toluene oxidation by at least 30°C.

Research has also focused on testing the durability of oxide supports in the presence of VOC mixtures. In fact, VOC mixtures are commonly found in industrial emissions originating from processes using organic solvents such as toluene, xylene and butanone. Other works are investigating the possible influence of one VOC on the removal of the other VOC in the same mixture. Nevertheless, only a few studies dealing with the oxidation of a mixture of VOCs (in particular toluene and butanone) have been published. For example, Beauchet et al.<sup>21</sup> showed that *o*-xylene inhibits the oxidation of isopropanol over NaX zeolite when both VOCs are present in the same mixture. They argued that *o*-xylene limits the access of isopropanol into the zeolite’s supercages and competes with propene (a byproduct of the oxidation of isopropanol) on the oxidation sites thus limiting its total oxidation. Burgos et al.<sup>22</sup> investigated the oxidation of toluene, 2-propanol and butanone (or methylethylketone, MEK) over Pt/metallic monoliths in three different situations: (a) separately, (b) a mixture of two of these VOCs and (c) a ternary mixture. They argued that mixing toluene and MEK did have an effect on the removal process owing to competitiveness between these molecules in their adsorption at the surface of the catalyst.

In a previously published paper, the effect of doping titania with vanadia has been investigated and proved to be efficient in boosting the resulting catalyst’s performance towards the oxidation of toluene. The same catalyst, named Pd5VTi, was investigated in this work in the oxidation of butanone (MEK), an oxygenated VOC, and in the removal of a butanone/toluene mixture. Results are compared to those of an undoped titania support, named PdTi, synthesized and tested under the same conditions. The main objectives were (a) to verify the effect of doping titania with vanadia on the removal of an oxygenated VOC and a mixture of two VOCs and (b) analyse through *operando* DIRFT coupled with mass spectrometry experiments the effect of mixing two VOCs on their removal by catalytic oxidation (to determine whether or not a competition exists between both VOCs).

## Experimental Section

### Synthesis procedures

**SYNTHESIS OF HIERARCHICALLY STRUCTURED DOPED MATERIALS.** Macromesoporous vanadium-doped titania supports were synthesized by a self-formation method. A homogeneous mixture of the alkoxide precursors  $\text{Ti}(\text{O}^i\text{Pr})_4$  (Sigma Aldrich 97%) and  $\text{OV}(\text{O}^i\text{Pr})_3$  (Sigma-Aldrich 98%)

based on a 5 at.% doping of  $\text{TiO}_2$  with vanadium, were added dropwise to water basified with  $\text{NH}_4\text{OH}$  ( $\text{pH} = 12$ ). The resulting oxide and the reaction liquid were transferred into an autoclave and subjected to solvothermal treatment (80 °C for 24 h). The product was then recovered by filtration, washed and dried at 60 °C prior to characterization. The prepared material was labeled 5VTi. Prepared materials were then calcined under air at 400 °C for 4 hours ( $1^\circ\text{C}\cdot\text{min}^{-1}$ ).<sup>5,20</sup>

The same procedure was also used for the preparation of the undoped  $\text{TiO}_2$  support.

**PREPARATION OF NOBLE METAL-LOADED CATALYSTS.** Pd catalysts supported by hierarchically porous doped and undoped titania were prepared using the aqueous impregnation method. A pre-determined amount of  $\text{Pd}(\text{NO}_3)_2$  (Alfa Aesar, 99.9%) solution was mixed with the support for 30 min such that the target impregnation was 0.5 wt% Pd. The water was then removed by roto-vaporation and the sample calcined under air ( $2\text{ L}\cdot\text{h}^{-1}$ ) at 400 °C for 4 h with a ramp rate of  $1^\circ\text{C}\cdot\text{min}^{-1}$ .<sup>20,23</sup> Prepared samples were labelled Pd5VTi and PdTi

### Catalyst Characterization

The specific surface areas ( $S_{\text{BET}}$ ) of the catalysts were measured by the BET method with a “ThermoElectron Qsurf Surface Area Analyzer” apparatus. The adsorption of a 30%  $\text{N}_2$  / 70% He mixture was carried out at  $-196^\circ\text{C}$ . Rapid heating of the sample resulted in desorption of the gaseous nitrogen that was then quantized with a thermal conductivity detector (TCD).

(Sub-ambient) temperature programmed reduction (TPR) profiles were recorded using an Altamira AMI-200 apparatus. Pd impregnated samples were heated from  $-40$  up to  $500^\circ\text{C}$ , at a heating rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$  in a flow of 5%  $\text{H}_2/\text{Ar}$  ( $30\text{ mL}\cdot\text{min}^{-1}$ ) and hydrogen consumption was monitored and integrated using thermal conductivity (TC) detection over the whole temperature range. Hydrogen consumption values per gram of the catalyst were defined as the necessary quantity of hydrogen needed to fully reduce the studied component present in the catalyst system.

Finally, the mass of Pd in each sample was quantified using inductively coupled plasma-optical emission spectroscopy (ICP-OES).

**CATALYTIC ACTIVITY.** The model pollutants toluene and butanone were chosen to represent aromatic and oxygenated VOCs respectively. The complete oxidation of each of these pollutants was performed over 100 mg of each catalyst in a conventional fixed bed reactor with a temperature rise of  $1^\circ\text{C}\cdot\text{min}^{-1}$ . The flow of VOC was set at 1000 ppm in a flow of air: with a total flow of  $100\text{ mL}\cdot\text{min}^{-1}$ . Prior to the oxidation reactions the catalysts were calcined at  $400^\circ\text{C}$  ( $1^\circ\text{C}\cdot\text{min}^{-1}$ ) in flowing air ( $2\text{ L}\cdot\text{h}^{-1}$ ), and then reduced under 5%  $\text{H}_2/\text{Ar}$  ( $2\text{ L}\cdot\text{h}^{-1}$ ) at  $200^\circ\text{C}$  ( $1^\circ\text{C}\cdot\text{min}^{-1}$ ) for 2 h. The products formed during combustion were analysed and quantified via gas chromatography using a CP-4900 microGC (Varian) coupled to a Pfeiffer-Vacuum Omnistar™ Quadrupole Mass Spectrometer (QMS) 205. Results presented as conversion graphs depict the

**Table 1** Theoretical and experimental hydrogen consumption values of PdTi and Pd5VTi measured by TPR experiments<sup>20</sup>

Samples	Theoretical H <sub>2</sub> Consumption (μmol.g <sup>-1</sup> )		Experimental H <sub>2</sub> consumption (μmol.g <sup>-1</sup> ) (corresponding temperature)			μmol of desorbed H <sub>2</sub> Negative peak
	Dopant	Pd	1 <sup>st</sup> peak	2 <sup>nd</sup> peak	Total	
Pd5VTi	667.2	75.2	61 (-11.7°C)	53.4 (163.5°C)	114.4	- 13.4
PdTi	-	75.2	96.6 (0.8°C)	-	96.6	- 10.4

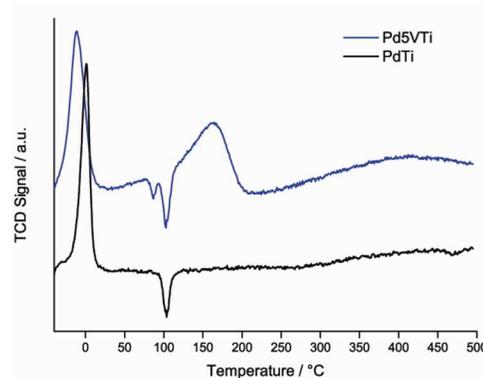
conversion of all the reaction products into CO<sub>2</sub>. The temperature at which a 50% conversion was achieved was then determined and constituted the main comparison tool.

*Operando* Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy was performed under the same test conditions as a typical catalytic test. It was conducted in the 1000-4000 cm<sup>-1</sup> range using an Equinox 55 Bruker spectrometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector, coupled to a CP-4900 microGC (Varian) to analyse the evolution of the oxidation reaction versus temperature. Mass spectrometry of the exiting gas flow was performed using a Pfeiffer-Vacuum Omnistar™ Quadrupole Mass Spectrometer (QMS) 205.

## Results and discussion

Previously published results showed the advantage of doping a macro-mesoporous titania support with niobium and vanadium oxides.<sup>20</sup> The doping process reduced T<sub>50</sub> values by at least 20°C for the total oxidation of toluene. After loading these materials with palladium, a sharp increase in the catalysts' activities was detected, with T<sub>50</sub> decreasing by 100°C for the V-doped sample. Overall, Pd5VTi proved to be the best performing catalytic system in the oxidation of toluene. TPR experiments showed reduction peaks at around 0°C related to the reduction of PdO species located at the surface of the material (figure 1). Another peak observed between 150 and 200°C corresponded to the reduction of PdO species found in bulky particles or stuck deep into the porous network. The latter showed a greater intensity for the doped sample compared to the undoped PdTi sample. Hydrogen consumption values related to each peak suggested an over-consumption of H<sub>2</sub> in the doped sample corresponding to the reduction of vanadium species as well as a small part of the support (Table 1).<sup>20</sup> An interaction between the active phase and the supported material

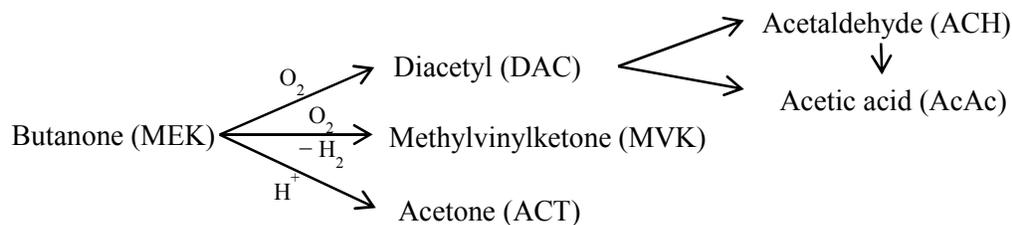
favoured by the presence of the dopant was proved to have been the cause of these TPR results. These results also explained the high activity seen for Pd5VTi in the oxidation of toluene, compared to the other catalysts used.

**Fig.1** TPR profiles of Pd5VTi and PdTi catalysts

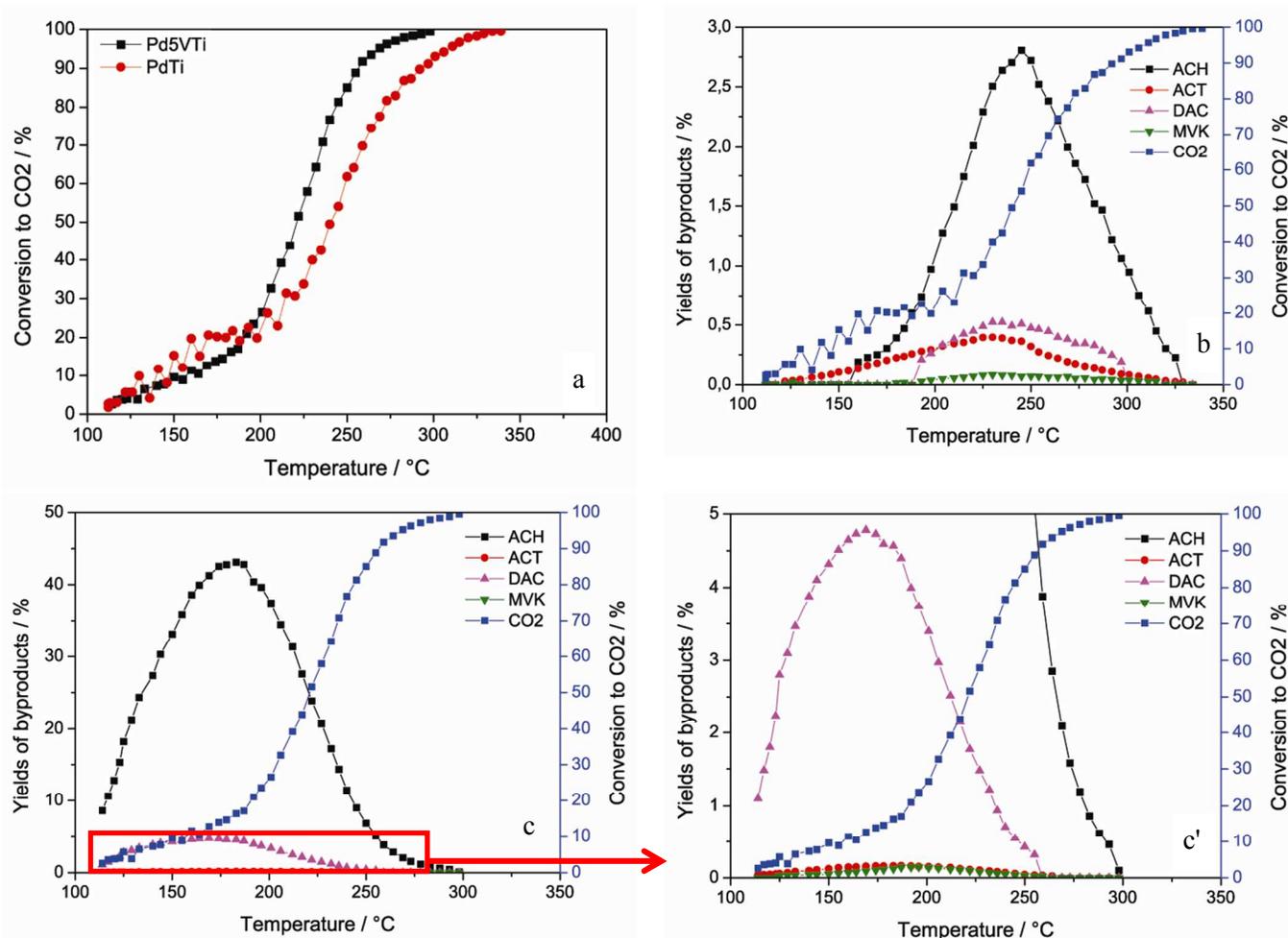
Furthermore, in another previous study, it was suggested that Pt-based systems are of more favourable use in the elimination of oxygenated VOC molecules compared to Pd-based catalytic systems. However, based on the above mentioned results, it was decided to test the Pd5VTi sample's ability to eliminate butanone (MEK), an oxygenated VOC. In addition, the elimination process of this molecule was analysed to try to determine important key factors interfering with the elimination process.

### Butanone oxidation

**GC CALIBRATION PROCESS.** In the literature, the elimination of butanone is believed to generate many by-products, 5 of which are considered to be major: acetaldehyde, methylvinylketone, diacetyl, acetone and acetic acid (scheme 1). Variations in the presence of acetic acid were detected by mass spectrometry (MS). However, quantifying the presence of acetic acid via this

**Scheme 1** Oxidation of butanone

method was impossible owing mainly to an overlapping of its specific peak and that of H<sub>2</sub>O (with great quantities of H<sub>2</sub>O formed in the exit stream of the oxidation reaction).

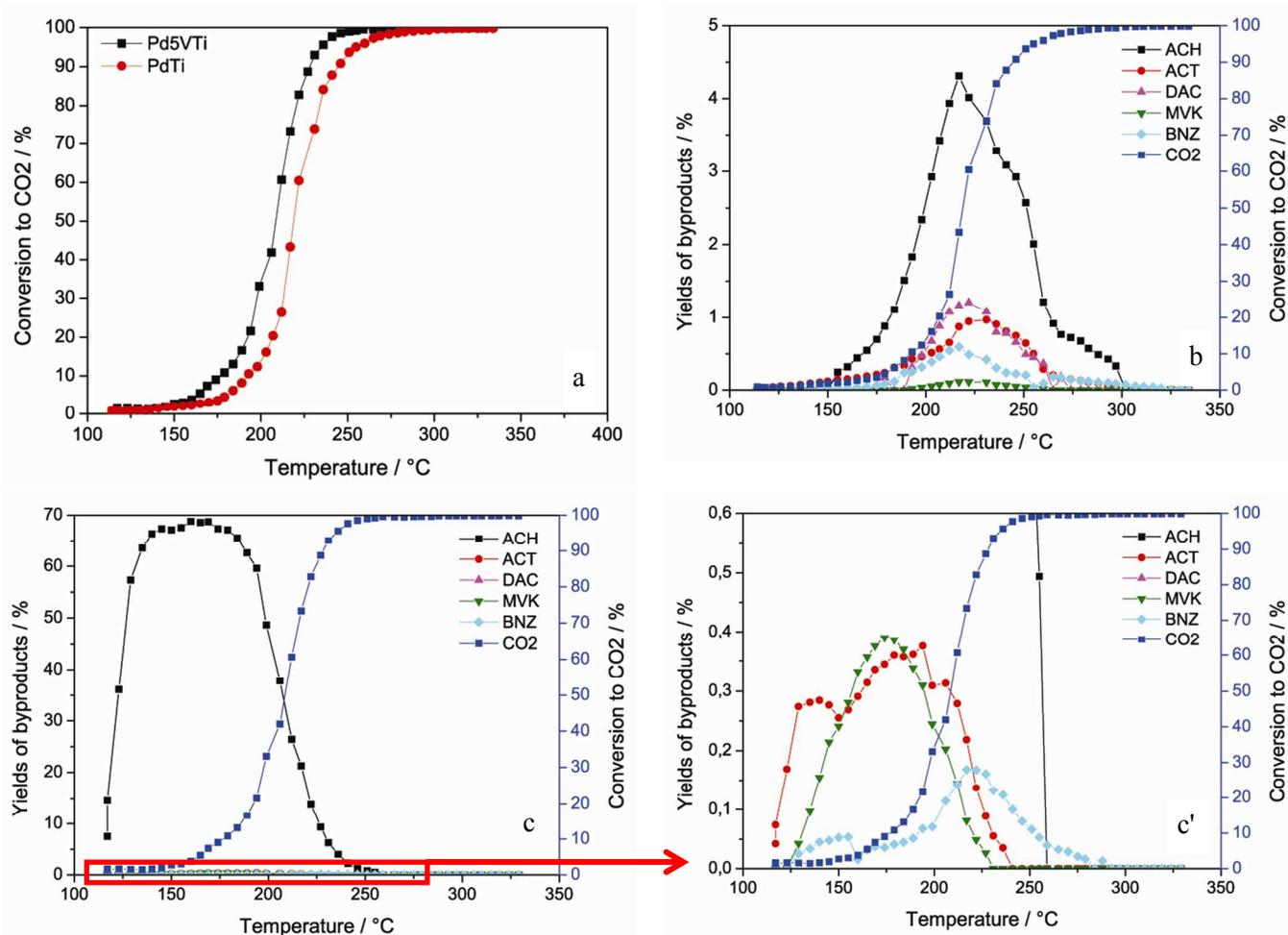


**Fig.2** Total oxidation of butanone over Pd5VTi and PdTi catalysts (a) and byproducts selectivity curves in PdTi (b) and Pd5VTi (c and c'). (ACH: acetaldehyde, ACT: acetone, MVK: methylvinylketone and DAC: diacetyl).

Therefore, the study did not include the formation of acetic acid. The remaining by-products were injected one by one at different temperatures as to elaborate a specific response factor to each product, thus quantifying their presence in the reaction exit streams.

**CATALYTIC TESTING.** Figure 2a shows conversion curves of butanone and all its by-products into CO<sub>2</sub> during catalytic oxidation over Pd5VTi and PdTi samples. It is obvious that the doped sample performed better than the undoped one, with a lower  $T_{50}$  of about 221°C (*cf* 234°C for PdTi). The slight increase in activity at around 20% conversion has previously been attributed to an exothermic reaction caused by the combustion of desorbed VOC molecules from the surface of the catalyst.<sup>23</sup> Selectivity curves shown in Figures 2b and c show the conversion of acetaldehyde (ACH), methylvinylketone (MVK), acetone (ACT) and diacetyl (DAC) into CO<sub>2</sub> as a function of the reaction temperature. These by-products are only formed before 100% conversion is achieved in both cases. The selectivity curves reveal that ACH is the major by-product formed during the course of the reaction. However, ACH yields

over Pd5VTi are 8 times higher than over PdTi, reaching nearly 40% at around 175°C. The peak of ACH formation is also shifted to lower temperatures for the doped sample. DAC yields were also 8 times greater for the Pd5VTi sample than for PdTi, and their formation was shifted to lower temperatures. According to Machold et al.,<sup>24</sup> when mixed with air or an oxygen rich atmosphere, MEK can be oxidized to DAC, which then breaks down into 2 acetaldehyde molecules. Furthermore, McCullagh et al.<sup>25</sup> argued MEK and oxygen molecules tend to compete for their adsorption on vanadium oxide (V<sub>2</sub>O<sub>5</sub>) adsorption sites, thus explaining the shift to lower temperatures. These two results combined together also provide an explanation for a greater formation of DAC and ACH over the doped sample. McCullagh et al.<sup>26</sup> also claimed that MVK molecules are formed by dehydrogenation of a reaction intermediate, 3-hydroxybutan-2-one, which is formed in an oxygen rich atmosphere. Finally, high yields of acetone were observed over the undoped catalyst. According to Machold et al.<sup>24</sup> and Yue et al.,<sup>27</sup> acetone is formed on strong acid sites. Therefore we can conclude that PdTi presents stronger acid sites than Pd5VTi. Moreover, surface area values presented in



**Fig.3** Total oxidation of the butanone/toluene mixture over Pd5VTi and PdTi catalysts (a) and byproducts selectivity curves over PdTi (b) and Pd5VTi (c and c'). (ACH: acetaldehyde, ACT: acetone, MVK: methylvinylketone, DAC: diacetyl, BNZ: benzene).

Table 2 are slightly decreased after catalytic testing. In previous reports, this decrease was attributed to the deposition of carbonaceous compounds at the surface of the used catalysts.<sup>5,28</sup> Hence, it is supposed that the reaction mechanisms happened at the surface of the catalyst, possibly through the adsorption of MEK and/or its reaction by-products at the surface of the used materials.

Even though the activity of the doped sample was higher than the undoped one in the total oxidation of butanone,  $T_{50}$  values for the oxidation of toluene were much lower than those for the elimination of MEK.<sup>20</sup> And since these two pollutants co-exist in many industrial emissions, it was decided to

investigate the elimination of both these molecules over both samples to understand the effect of mixing VOC molecules on the catalysts' durability.

Figure 3 shows the conversion curves of both VOCs and their by-products into  $\text{CO}_2$ . As observed in the oxidation of butanone, Pd5VTi showed a better activity than PdTi with a  $T_{50}$  of about 208°C (Fig.3a). Both catalysts also proved to be more active than what was recorded in the oxidation of butanone and Pd5VTi showed a similar activity to that observed in the oxidation of toluene (Table 2) in a previously published work.<sup>20</sup> These catalysts were also found to be more active than many Pd-loaded  $\text{TiO}_2$  catalysts (commercial or prepared by methods other than the auto-formation used herein) tested in the oxidation of toluene. For example, works published by Garcia et al.,<sup>29</sup> Santos et al.,<sup>30</sup> Tidahy et al.,<sup>31,32</sup> Hosseini et al.<sup>23</sup> presented different  $T_{50}$  values in the total oxidation of toluene over Pd/ $\text{TiO}_2$  materials, the lowest value being around 220°C,<sup>30</sup> making both catalysts used in this work more efficient in the oxidation of toluene as an individual VOC, and in a mixture with butanone. Same as after the other catalytic tests, a limited

**Table 2** Surface area measurements and  $T_{50}$  values recorded for both catalysts after catalytic testing

Samples	$S_{\text{BET}}$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )				$T_{50}$ (°C)		
	Before testing	After BUT	After TOL	After Mixture	BUT	TOL	Mixture
Pd5VTi	159	155	135	137	221	201	208
PdTi	163	144	152	130	234	204	219

decrease in  $S_{\text{BET}}$  values was detected after the oxidation reaction. This is mainly indicative of the presence of carbonaceous compounds at the surface of the used materials.

Selectivity curves presented in Figures 3b, c and c' show in general, an increase in by-product formation. With both catalysts, acetaldehyde formation was nearly double that which was observed in the oxidation of butanone. In fact, tests over the PdTi sample showed an increase in the formation of all potential by-products, with a significant presence of benzene, provided by the degradation of toluene molecules.<sup>5</sup> Mass spectrometry experiments showed that in the oxidation of butanone alone, a partial breakdown of MEK molecules has been observed, MEK being the last VOC to be eliminated from the stream. However, in the oxidation of the mixture, butanone was completely broken down to by-products during the course of the reaction. Benzene was the last VOC to be eliminated before 100% conversion was reached. In the literature, Lahousse et al.<sup>33</sup> argued that, in a gaseous stream composed of a VOC mixture, oxygenated VOCs are difficult to oxidise. Thus, when these molecules are adsorbed at the surface of the catalyst they participate in the increase in reaction temperature values. Sanz et al.<sup>34</sup> claimed that this increase was mainly caused by competitiveness between VOC molecules present in the same mixture. In their work on the elimination of a toluene-ethyl acetate mixture over a Pt-OMS-2 catalyst, they noticed that ethyl-acetate inhibited the adsorption and oxidation of toluene. Based on works by Blasin-Aubé et al.<sup>35</sup>, they concluded that molecules compete in a way that the first component to be adsorbed on the catalyst is the most easily oxidised. These arguments combined with other results published by Papaefthimiou et al.<sup>36</sup> unanimously agree that competition between VOC molecules results in an increase in temperature values, which is the opposite of what was observed in the present work. In fact, it was clear that the presence of toluene facilitated the decomposition of butanone molecules and consequently, its elimination from the gas stream.

As for the Pd5VTi sample, a 68% yield of ACH was detected between 140°C and 175°C, whereas yields of the remaining by-products fell significantly. This dramatic increase in the formation of acetaldehyde explains the reduction in the  $T_{50}$  value after the oxidation of the VOC mixture. However, the decrease in the formation of other by-products suggests either a limited adsorption time of VOC molecules onto the sample or a lack of adsorption sites. In fact, butanone oxidation follows the Langmuir-Hinshelwood and Mars-van Krevelen models.<sup>37</sup> However Raillard et al.<sup>38</sup> and Vincent et al.<sup>39</sup> proved the predominance of the Langmuir-Hinshelwood mechanism in the photocatalytic elimination of MEK over titania supports. Therefore, the transformation of MEK into complex by-products is dependent upon the adsorption time and sites. Two possible reasons as to why by-product formation sharply decreased can be made: (a) competitiveness between VOC molecules and also between  $O_2$  and VOCs, (b) formation of complex carbonaceous compounds or coke molecules at the surface of the catalysts. In the first case (a), competition might play a role in reducing adsorption time, thus limiting the formation of reaction intermediates at the surface of the catalyst, whereas coke deposition (b) at the surface of the catalyst can temporarily block active sites thus affecting the transformation of butanone. Since only a limited number of studies discussed competitiveness between VOC molecules in the oxidation of a VOC mixture and in order to verify which of the above mentioned hypotheses is closest to reality, *in-situ operando* DRIFT experiments were conducted during the course of the reaction. A mass spectrometer was linked to a microGC to analyse the variations in concentration of the products and by-products of catalytic oxidation in the gaseous stream.

A flow of air and butanone (1000 ppm) was injected into the system, then after 10 mins of exposure, toluene (1000 ppm) was added to the stream. This method is used to (a) detect spectral bands specific to butanone without the interference of

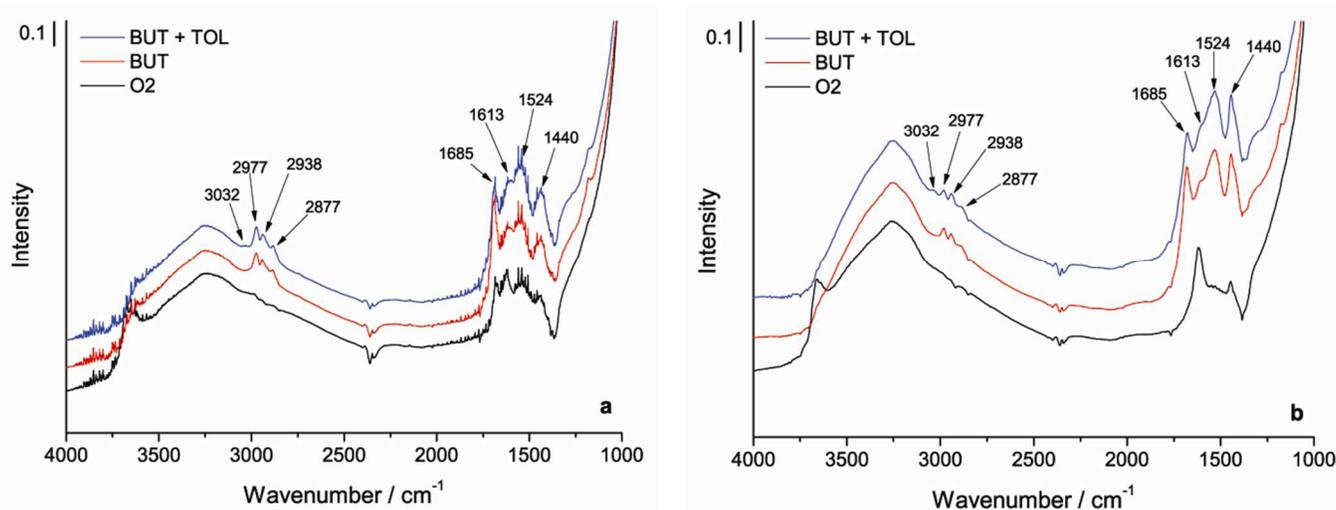


Fig.4 FTIR spectra of (a) PdTi and (b) Pd5VTi samples exposed to air ( $O_2$ ), butanone (BUT) and the VOC mixture (BUT + TOL)

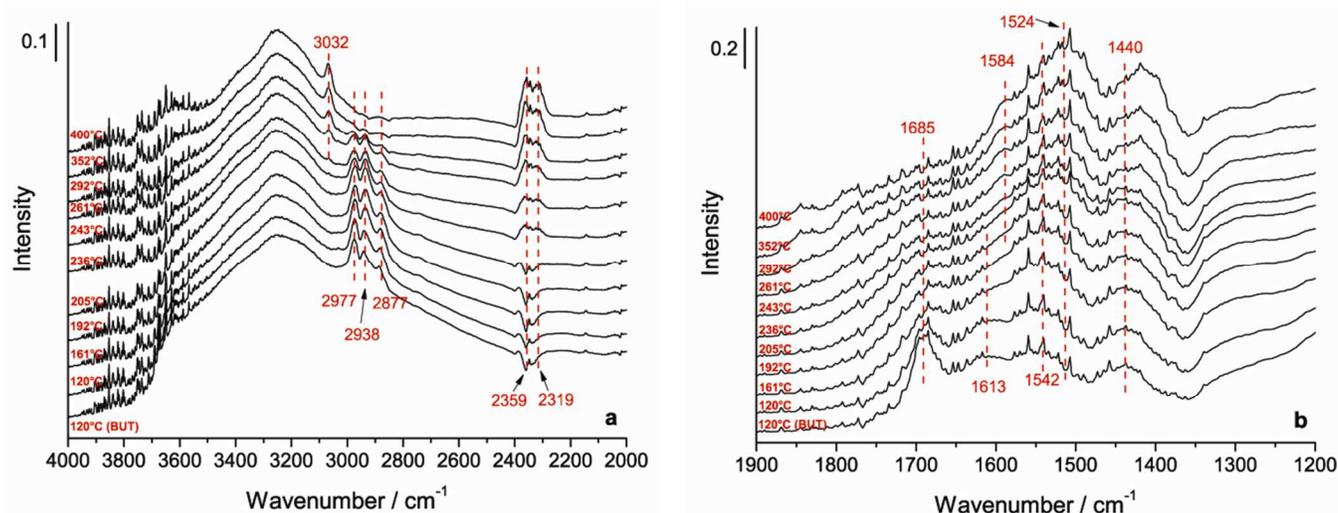


Fig.5 FTIR spectra of PdTi catalyst used in the oxidation of the butanone/toluene mixture

toluene molecules, and (b) witness the possible existence of competitive adsorption behaviour between toluene and butanone molecules at the surface of each catalyst. Figures 4a and 4b illustrate spectral bands recorded over PdTi and Pd5VTi respectively and assignments for each band are shown in Table 3. Spectral bands situated between 2980 and 2880  $\text{cm}^{-1}$  are related to methyl radicals in toluene (2977  $\text{cm}^{-1}$ ) and methyl and ethyl radicals in butanone (2977, 2938 et 2877  $\text{cm}^{-1}$ ), whereas toluene's aromatic C–H bonds vibrate at 3032  $\text{cm}^{-1}$ . After toluene was injected into the stream, a decrease in the intensity of the 1685  $\text{cm}^{-1}$  spectral band was observed. According to Manríquez et al.,<sup>40</sup> this band is correlated to the vibration of C=O bonds. So the observed reduction in intensity could relate to the desorption of butanone or other molecules containing this bond. Therefore the existence of a competitive effect between toluene and butanone molecules has been revealed. Irusta et al.<sup>41</sup> proved the presence of this competition by feeding both toluene and butanone simultaneously into the reactor stream over La-based perovskites. They proved that the competitive effect lies in the interaction of both VOCs with the catalyst surface.

Table 3 IR absorption bands of PdTi and Pd5VTi (shown in figures 4, 5 and 6) and their corresponding assignments

PdTi Band ( $\text{cm}^{-1}$ )	Pd5VTi Band ( $\text{cm}^{-1}$ )	Assignment
3500-3100	3500-3100	O–H (Ti–OH)
3032	3032	C–H (aromatic ring)
2977, 2938, 2877	2977, 2938, 2877	C–H $\text{sp}^3$
2359	-	$\text{CO}_2$
2316	-	Adsorbed $\text{CO}_2$
-	2215	C=C
1685	1685	C=O
1613	1613	C=C connected to –C=O bonds
1584	-	C=C in ring
1524	1524	C–C olefin
1507	-	C–C aromatic
-	1476	C=C ring stretch
1440	1440	C–O–H

Figures 5a and 5b show IR spectra of PdTi during the oxidation of the butanone/toluene mixture. First of all, a decrease in the intensity of spectral bands related to butanone is observed over the course of the reaction (Fig.5a). Meanwhile, and at temperatures higher than 236°C, bands related to toluene's aromatic C–H bonds appear with intensities increasing proportionally to temperature values. This observation was accompanied by a decrease in toluene and an increase in the presence of benzene observed by mass spectrometry (MS). The spectral band at 1584  $\text{cm}^{-1}$  appearing at high temperatures corresponds to the adsorption of aromatic rings at the surface of the catalyst. Accordingly, its presence suggests that benzene and toluene molecules are adsorbed at the surface of the PdTi catalyst. However, the intensities of bands specific to toluene methyl radicals also decrease with increasing temperatures. Therefore, it can be concluded that methyl radicals are provided by the decomposition of toluene molecules into benzene and that the latter molecules are adsorbed at the surface of the catalyst.

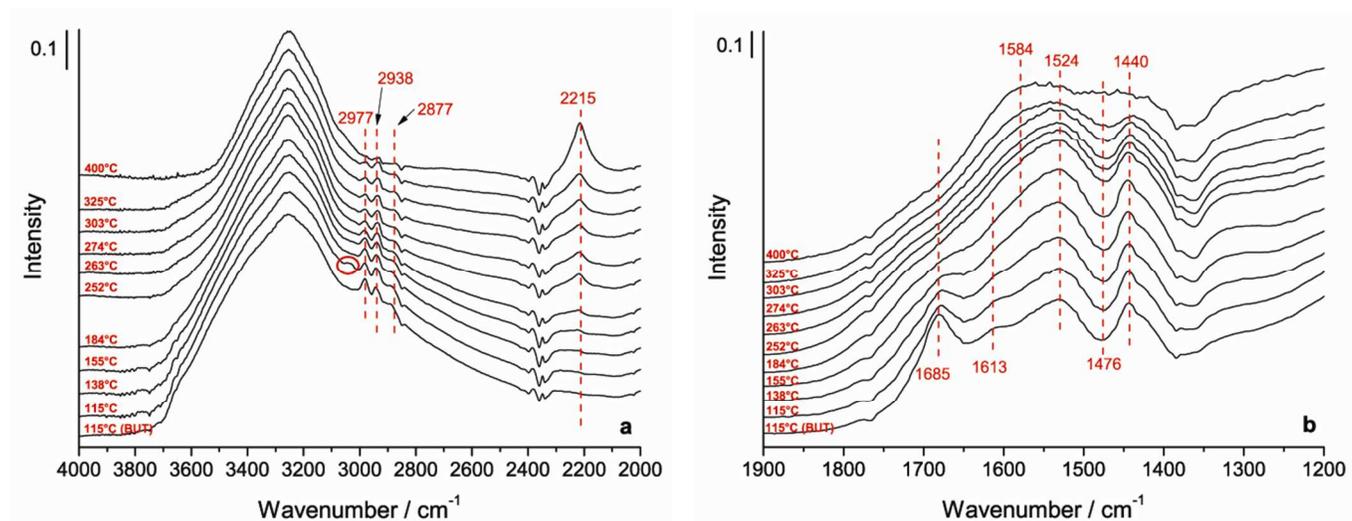


Fig.6 FTIR spectra of Pd5VTi catalyst used in the oxidation of the butanone/toluene mixture

The band situated at  $1685\text{ cm}^{-1}$  decreases in intensity along with the bands related to butanone in Figure 5a. According to Ross<sup>42</sup> and Stuart<sup>43</sup> this band corresponds to the vibration of C=O bonds. Its reduction suggests a reduction in the number of these bonds. Simultaneously, MS results showed an increasing presence of acetaldehyde, acetic acid and 1-pent-3-one. This last by-product is produced by the chemical substitutions and rearrangements taking place at the surface of the catalyst, as discussed by Yue et al.<sup>27</sup> Even  $\text{CO}_2$  molecules have been detected on the surface of PdTi. Therefore it can be concluded that, even at 100% conversion, reactions are still occurring at the surface of PdTi, and carbonaceous compounds are thus formed and possibly deposited at the surface of this material.

DRIFT results for Pd5VTi illustrated in Figures 6a and b show progressive reductions in the intensity of butanone specific bands throughout the oxidation reaction ( $2977$ ,  $2938$  and  $2877\text{ cm}^{-1}$  Figure 6a and  $1685\text{ cm}^{-1}$  Figure 6b). MS results show an increasing presence of  $\text{CO}_2$  and acetaldehyde, and less significant presence of acetone. Both simultaneous results are in accordance with selectivity graphs discussed earlier. They also prove that the decomposition of butanone occurs as early as  $138^\circ\text{C}$ . Another significant result is observed in Figure 6a; the band corresponding to toluene aromatic C–H bonds is detected only at  $T=138^\circ\text{C}$ , although MS results show a slight presence of benzene. Burgos et al.<sup>22</sup> proved through TPD results that when toluene and MEK are mixed, the adsorption of toluene at the surface of a Pt/metallic monolith catalyst decreases in favour of MEK. They also argued that by-products of the partial oxidation of toluene were eliminated more easily owing to variations in the temperature of the catalyst surface. These variations are caused by the exothermic nature of the oxidation of VOCs adsorbed at the surface of the catalyst. Therefore, it can be concluded that doping with vanadium enhanced the adsorption rate of MEK molecules at the surface

of Pd5VTi compared to toluene. The oxidation of MEK molecules is achieved according to a Langmuir-Hinshelwood mechanism whereas toluene oxidation follows a Mars-Van Krevelen type mechanism.<sup>37</sup> Consequently, this competitiveness towards oxygen species available at the surface of the used material enhances the materials performance towards the oxidation of both molecules. Finally, both catalysts witnessed a deposition of carbonaceous compounds at their surfaces. However, based on *operando* DRIFT results, it is believed that higher amounts of coke were deposited on PdTi than on Pd5VTi, owing to (a) the lower resolution of PdTi spectra at high temperatures and more predominantly (b) the clear presence of radicals at the surface of PdTi.

## Conclusion

The effect of doping a titania catalytic support with vanadium oxide has been analysed in this work. The resulting Pd loaded catalyst proved to be efficient in the removal of butanone as well as a mixture of butanone and toluene. The presence of vanadium prompts competitiveness between butanone and oxygen molecules in terms of adsorption at the surface of the catalyst. However in the presence of toluene, butanone shows a higher affinity to the surface of the catalyst, thus ensuring a faster oxidation process than when alone in the gaseous stream. This was achieved through a faster decomposition of butanone into its major reaction by-products. This decomposition varies with the nature of the support. *Operando* DRIFT results showed that the presence of vanadium ensures different elimination mechanisms

for toluene and butanone, thus enhancing their competitiveness. In the absence of vanadium species, both molecules tend to adsorb on the surface of the catalyst. This participates in the formation of reaction intermediates, and consequently, VOC molecules are even harder to totally eliminate.

## Acknowledgements

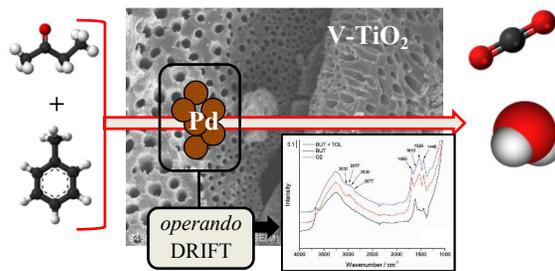
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## Table of content

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