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# Influence of zirconia addition in TiO<sub>2</sub> and TiO<sub>2</sub>–CeO<sub>2</sub> aerogels on the textural, structural and catalytic properties of supported vanadia in chlorobenzene oxidation

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This paper studies the effect of the direct incorporation of ZrO<sub>2</sub> in TiO<sub>2</sub> and TiO<sub>2</sub>–CeO<sub>2</sub> aerogel supports prepared by sol–gel route on the physico–chemical and catalytic properties of supported vanadia catalysts in the total oxidation of chlorobenzene. The obtained catalysts have been characterized by means of ICP–AES, N<sub>2</sub> adsorption–desorption at 77 K, XRD, XPS, H<sub>2</sub>–TPR and NH<sub>3</sub>–TPD. The results revealed that Zr-doped V<sub>2</sub>O<sub>5</sub> based catalyst is beneficial for the improvement of catalytic properties in chlorobenzene total oxidation. In particular, in the absence of cerium groups, this beneficial effect is correlated with the better acidic properties or/and the stabilization of the V<sub>2</sub>O<sub>5</sub> active phase in a higher oxidation state. However, in the case of cerium rich catalyst, this positive effect is much stronger thanks to the enhanced redox properties of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>–CeO<sub>2</sub>–ZrO<sub>2</sub>.

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## 1. Introduction

Vanadia based TiO<sub>2</sub> materials constitute a very important class of catalytic materials resistant against chlorinated volatile organic compounds (Cl–VOCs) released in the atmosphere.<sup>1–5</sup> The latter have been considered to be very toxic, carcinogenic and environmentally persistent organic pollutants.<sup>3,6,7</sup> The catalytic destruction of chlorinated VOCs to CO<sub>x</sub>, H<sub>2</sub>O, HCl and Cl<sub>2</sub> appears as a very promising solution since it allows destroying these pollutants without deactivation of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts by chlorine poisoning on their surfaces.<sup>3</sup>

Besides, we have demonstrated that the direct incorporation of cerium species in the TiO<sub>2</sub> aerogel support prepared by the sol gel route has generated great interest in the catalytic performances of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst in the total oxidation of chlorobenzene.<sup>8</sup> The success of the use of cerium oxide as a promoter of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> material is due to its oxygen storage and reduction/oxidation properties.<sup>9–11</sup> In fact, labile oxygen vacancies and bulk oxygen species with relatively high mobility are easily formed during the redox shift between Ce<sup>3+</sup> and Ce<sup>4+</sup> under oxidizing and reducing conditions. The mechanism of the oxidation reactions of Cl–VOCs over ceria is usually considered to be of the redox or Mars and van Krevelen type.

The key step of this mechanism is that CeO<sub>2</sub> supplies active oxygen to the vanadium species that are reduced during the catalytic reaction.<sup>8</sup>

However, the capabilities of the redox couple Ce<sup>4+</sup>/Ce<sup>3+</sup> could be strongly enhanced if other elements are introduced into the CeO<sub>2</sub> lattice. Among various elements, the introduction of zirconium in the lattice of CeO<sub>2</sub> is particularly effective in the enhancement of the storage/release capacity and redox properties of CeO<sub>2</sub>.<sup>12,13</sup>

On the other hand, the combined TiO<sub>2</sub>–ZrO<sub>2</sub> mixed oxide has also attracted considerable attention recently as active catalyst as well as support for a wide variety of catalytic applications.<sup>14–20</sup> In fact, it is established in the literature that mixing these two dissimilar oxides could lead to totally different physico–chemical properties and catalytic behavior since they are liable to form new stable compounds.<sup>21</sup> Such advanced titania–zirconia mixed oxides not only take advantage of both TiO<sub>2</sub> (active catalyst and support) and ZrO<sub>2</sub> (acid–base properties), but also extend their application through the generation of new catalytic sites due to a strong interaction between them.<sup>21</sup> In fact, the facile formation of zirconium titanate (ZrTiO<sub>4</sub>) compound between ZrO<sub>2</sub> and TiO<sub>2</sub> allows excellent catalytic properties for various reactions.<sup>21</sup>

Therefore, given the favorable characteristics of zirconia, the aim of this work is to study the effect of the direct incorporation of ZrO<sub>2</sub> in TiO<sub>2</sub> and TiO<sub>2</sub>–CeO<sub>2</sub> aerogel supports prepared by sol–gel route on the physico–chemical and catalytic properties of supported vanadia catalysts in the total oxidation of chlorobenzene.

To determine the physico–chemical properties of various samples elaborated, different characterization techniques

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namely, BET surface area, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD), temperature-programmed reduction (TPR) with  $\text{H}_2$ , temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) and *in situ* diffuse reflectance infrared spectroscopy (DRIFTS) were employed.

## 2. Experimental

### 2.1 Elaboration of catalysts

$\text{TiO}_2$ ,  $\text{TiO}_2\text{-ZrO}_2$ ,  $\text{TiO}_2\text{-CeO}_2$  and  $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$  supports were prepared *via* sol-gel method as follows: titanium(IV) isopropoxide (Aldrich, 98%), as precursor, with anhydrous ethanol (Aldrich, 98%), as solvent, was chemically modified by adding acetylacetone (Fluka, 99%) according to a molar ratio acetylacetone/Ti = 1 in order to control hydrolysis and condensation reaction rates. This solution was maintained for 1 h under stirring. To obtain mixed oxides, cerium nitrate (Aldrich, 99.5%) or/and zirconium acetylacetonate (Aldrich, 98%) were added to titanium isopropoxide according to molar ratios Ce/Ti = 0.1 and Zr/Ti = 0.1. Homogenous gels are obtained by hydrolysis and condensation after  $\text{HNO}_3$  supply. The amount of distilled water added corresponded to the molar ratio  $\text{H}_2\text{O/Ti} = 10$ . The gels were thereafter transformed into aerogels by drying under supercritical conditions of ethanol ( $P = 63$  bars,  $T = 243$  °C).

Catalysts with nominal vanadia loading of 2 wt% were elaborated by impregnating 2 g of support with 4 ml of an acetone solution of vanadyl acetylacetonate (Fluka, 95%).

The obtained solids are then dried in an oven at 60 °C for 24 h. Finally, catalysts are calcined for 3 h at 500 °C under flowing  $\text{O}_2$  (30 ml min<sup>-1</sup>) and denoted respectively VTi, VTiZr, VTiCe and VTiCeZr.

### 2.2 Characterization of catalysts

**2.2.1 Elemental analysis.** The elemental analysis was performed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) allowing estimating the weight percentage of Ce, Zr and V. These measurements were performed on a Horiba Jobin Yvon apparatus, Model Activa.

**2.2.2  $\text{N}_2$  adsorption-desorption at 77 K.** Specific surface area and pore volume measurements of the samples were done by  $\text{N}_2$  physisorption at 77 K using a Micromeritics ASAP 2020 apparatus. Prior to  $\text{N}_2$  physisorption, the samples were out-gassed in vacuum during 6 h at 200 °C.

**2.2.3 X-ray diffraction (XRD).** X-ray diffraction patterns (XRD) were obtained using a MRD PRO PANalytical X'Pert PRO instrument with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418$  Å) at the rate of 0.02° per s from 5 to 70°.

**2.2.4 X-ray photoelectron spectroscopy (XPS).** X-ray photoelectron spectra (XPS) were collected on a SSI X probe spectrometer (model SSI 100, Surface Science Laboratories, Mountain View, CA, USA) equipped with a monochromatized  $\text{AlK}_{\alpha}$  radiation (1486 eV). The samples powders, pressed in small stainless-steel troughs of 4 mm diameter, were placed on an insulating homemade ceramic carousel. The pressure in the

analysis chamber was around  $10^{-6}$  Pa. The angle between the surface normal and the axis of the analyser lens was 55°. The analysed area was approximately 1.4 mm<sup>2</sup> and the pass energy was set at 150 eV. The C 1s peak of carbon has been fixed at 284.8 eV to set the binding energy scale. Data treatment was performed with the CasaXPS program (Casa Software Ltd, UK) and some spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a non-linear baseline.

**2.2.5 Temperature programmed desorption of ammonia ( $\text{NH}_3$ -TPD).** Total acidity was evaluated by temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) using a quadrupole Balzers QMC 311. Before  $\text{NH}_3$  desorption, the samples were pre-treated under He flow (60 ml min<sup>-1</sup>) at 200 °C for 1 h.  $\text{NH}_3$  adsorption was performed under ambient conditions by flowing 0.5%  $\text{NH}_3$  in He over the catalyst until saturation and then following the desorption of  $\text{NH}_3$  along a temperature-programmed treatment under He from 50 to 500 °C using a heating rate of 10 °C min<sup>-1</sup>.

**2.2.6 Temperature programmed reduction of  $\text{H}_2$  ( $\text{H}_2$ -TPR).** Temperature programmed reduction (TPR) experiments were performed in a dynamic apparatus using 5%  $\text{H}_2$  in He flowing at 60 ml min<sup>-1</sup>. Experiments were carried out in the range 30–800 °C. The inlet and outlet gas compositions were measured using a quadrupole mass spectrometer QMC 311 Balzers coupled to the reactor.

### 2.3 Catalytic test

Catalytic tests were performed with 200 mg of catalyst (200–315 µm) diluted in 800 mg of inactive glass spheres with diameters in the range 315–500 µm in a metallic fixed-bed micro-reactor (PID Eng&Tech, Madrid, Spain) operating at atmospheric pressure and fully monitored by computer. The gas stream was composed of 100 ppm of chlorobenzene, 20 vol% of  $\text{O}_2$  and helium as diluting gas to obtain 200 ml min<sup>-1</sup> (space velocity (V<sub>VH</sub>) = 37 000 h<sup>-1</sup>). The reaction was run from 100 to 400 °C by steps of 50 °C. At each temperature investigated, the catalyst was stabilized for 150 min in order to reach steady state. Analysis of the reactants and products was continuously performed by on line gas chromatography (GC). The GC allowed chlorobenzene,  $\text{O}_2$ , CO, and  $\text{CO}_2$  to be quantified and other chlorohydrocarbons to be detected. To calculate the conversion, only the concentrations of the reactants and products measured after stabilization and averaged in a period of time from 100 to 150 minutes were taken into account. The measured performances were accurate within a range of about 1% (in relative) for the conversion of chlorobenzene. Analysis of reactants and products was continuously performed by on line gas chromatography (GC).

## 3. Results and discussion

### 3.1 Elemental analysis

Nominal and experimental chemical compositions of the VTi, VTiZr, VTiCe and VTiCeZr samples are compared in Table 1.



**Table 1** Element analysis and theoretical composition of VTi, VTiCe, VTiZr and VTiCeZr calcined at 500 °C

Catalyst	Bulk composition (wt%)			Nominal composition (wt%)		
	V	Ce	Zr	V	Ce	Zr
VTi	1.6			1.1		
VTiCe	1.08	14.22		1.1	14.4	
VTiZr	0.99		12.34	1.1		12.4
VTiCeZr	1.02	14.36	12.23	1.1	14.4	12.4

The results indicate a good agreement with the nominal compositions revealing that vanadium, zirconium and cerium were successfully incorporated in the catalysts. The small difference observed may result from inaccuracies in the preparation of the solution of samples for ICP analysis (*ca.* weighing).

### 3.2 N<sub>2</sub>-adsorption-desorption at 77 K

The specific surface areas and pore diameters of TiO<sub>2</sub>, TiO<sub>2</sub>-ZrO<sub>2</sub>, TiO<sub>2</sub>-CeO<sub>2</sub> and TiO<sub>2</sub>-CeO<sub>2</sub>-ZrO<sub>2</sub> aerogel supports (as references) and VTi, VTiZr, VTiCe and VTiCeZr catalysts, calcined at 500 °C are given in Table 2.

All solids are classified as mesoporous materials (pores between 20 and 500 Å) and exhibited specific surface areas higher than industrial TiO<sub>2</sub> such as TiO<sub>2</sub> Degussa P 25, which is a mixture of anatase (70%) and rutile (30%) and which has a surface area of 50 m<sup>2</sup> g<sup>-1</sup>.<sup>22</sup>

From Table 2, it can be seen that specific surface area of aerogel TiO<sub>2</sub> support synthesized by one-pot sol-gel method appeared to depend only on the cerium content. In fact, CeO<sub>2</sub> is beneficial for the specific surface area of TiO<sub>2</sub> aerogel which increases from 115 m<sup>2</sup> g<sup>-1</sup> to 140 m<sup>2</sup> g<sup>-1</sup> after incorporation of ceria. However, doping TiO<sub>2</sub> with ZrO<sub>2</sub> allows preserving its pristine specific surface area.

Furthermore, the TiO<sub>2</sub>-CeO<sub>2</sub> sample exhibits specific surface area of 140 m<sup>2</sup> g<sup>-1</sup>. A steady decrease from 140 to 94 m<sup>2</sup> g<sup>-1</sup> is observed in the case of TiO<sub>2</sub>-CeO<sub>2</sub>-ZrO<sub>2</sub> aerogel support. The observed decrease could be due to the penetration of the dispersed zirconium oxide into the pores of TiO<sub>2</sub>-CeO<sub>2</sub> support, thereby narrowing its pore diameter and blocking some of the pores.<sup>23</sup>

**Table 2** Specific surface areas and mean pore size diameters of supports and catalysts calcined at 500 °C

Sample	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore diameter (Å)
TiO <sub>2</sub>	115	80
TiO <sub>2</sub> -CeO <sub>2</sub>	140	174
TiO <sub>2</sub> -ZrO <sub>2</sub>	110	137
TiO <sub>2</sub> -CeO <sub>2</sub> -ZrO <sub>2</sub>	94	134
VTi	136	98
VTiCe	141	114
VTiZr	128	139
VTiCeZr	102	95

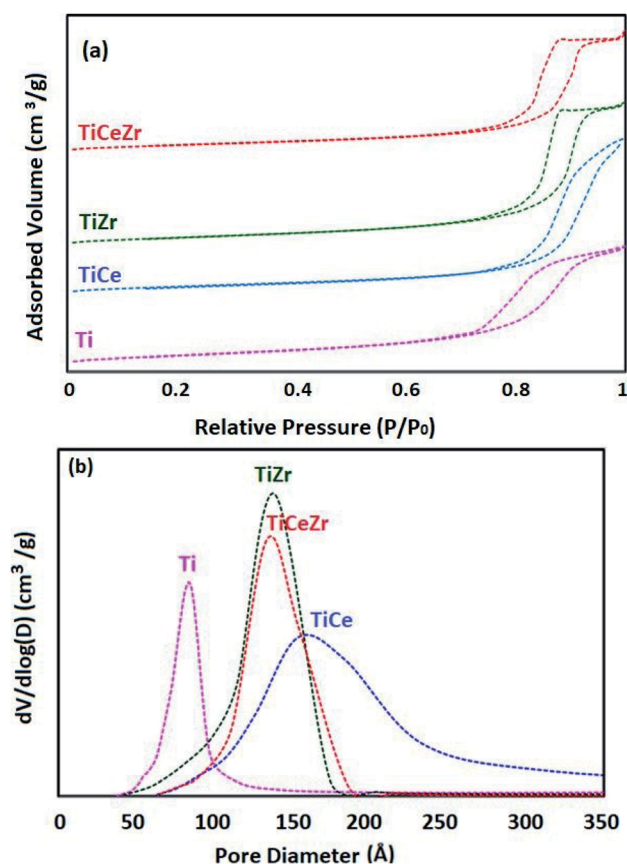
On the other hand, vanadia based materials were found to display greater or quiet similar specific surface area than TiO<sub>2</sub>, TiO<sub>2</sub>-ZrO<sub>2</sub>, TiO<sub>2</sub>-CeO<sub>2</sub> and TiO<sub>2</sub>-CeO<sub>2</sub>-ZrO<sub>2</sub> supports. It is probable that this effect is due to the elaboration route of vanadia based materials which occurs in two steps.

N<sub>2</sub> adsorption-desorption isotherms at 77 K and pore size distribution curves of Ti, TiCe, TiZr, TiCeZr (as references) and VTi, VTiCe, VTiZr and VTiCeZr are displayed in Fig. 1 and 2, respectively. According to the IUPAC classification,<sup>24</sup> all the samples are characterized by the type IV isotherms (behavior characteristic of mesoporous materials) with hysteresis loops type H1 characteristic of porous materials.<sup>24</sup>

It is clearly seen from the pore size distribution curves of the supports that the modification of TiO<sub>2</sub> by CeO<sub>2</sub>, ZrO<sub>2</sub> or CeO<sub>2</sub>-ZrO<sub>2</sub> contributes to the enlargement of its pores. The observed increase in the diameter of pores could result from the combination of different pore sizes derived from TiO<sub>2</sub> particle and TiO<sub>2</sub>-ZrO<sub>2</sub> or TiO<sub>2</sub>-CeO<sub>2</sub> particle on the other hand.<sup>25,26</sup>

After vanadium impregnation, the average pore diameter of TiO<sub>2</sub> increases leading to clear changes in the textural properties. These results could be attributed to the reorganization of TiO<sub>2</sub> crystallites sizes after vanadium impregnation.<sup>27</sup>

In the case of ceria rich catalysts, a decrease in the average pore diameter is observed which could be due to the plugging of the small pores by cerium incorporation.<sup>28</sup> On the contrary, V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-ZrO<sub>2</sub> samples had narrow BJH pore

**Fig. 1** Textural properties of Ti, TiCe, TiZr and TiCeZr supports: (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore size distribution curves.



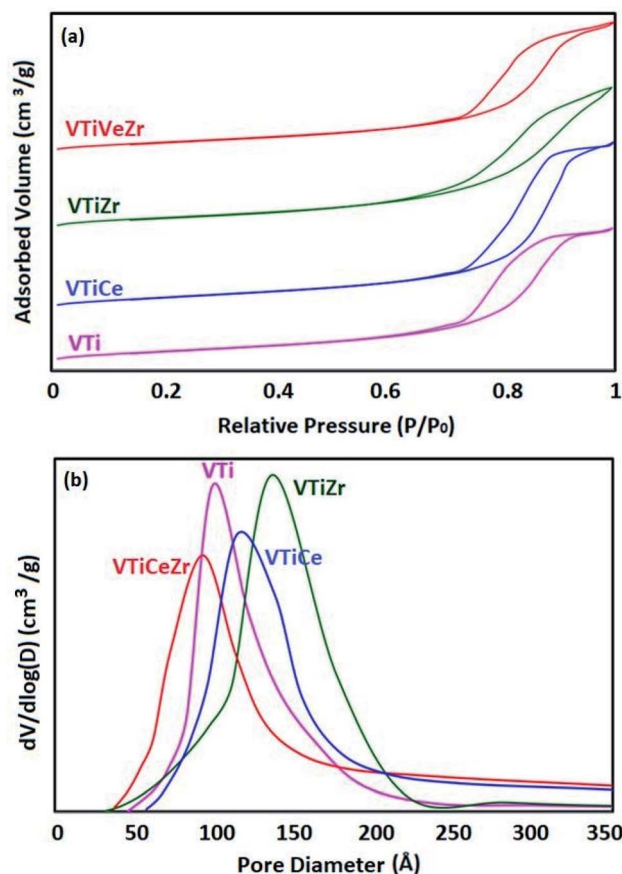


Fig. 2 Textural properties of VTi, VTiCe, VTiZr and VTiCeZr supports: (a)  $N_2$  adsorption-desorption isotherms and (b) pore size distribution curves.

size distributions with diameters centered at 137 Å and 139 Å (Table 2), demonstrating that the doping of zirconium stabilized the mesoporous structure.<sup>29</sup>

### 3.3 X-ray diffraction

The XRD patterns of VTi, VTiZr, VTiCe and VTiCeZr samples calcined at 500 °C are shown in Fig. 3. Only the broad diffraction lines due to  $TiO_2$  anatase with high crystallinity such as  $2\theta = 25^\circ, 37^\circ, 48^\circ$  and  $53^\circ$  (PDF-ICDD 21-1272) plus a few peaks belonging to cubic  $CeO_2$  at  $2\theta = 28.5^\circ, 33.3^\circ$  and  $47.4^\circ$  (PDF 00-034-0394) are identified.

The absence of characteristic lines of  $ZrO_2$  at  $2\theta$  values around  $28.2^\circ, 31.5^\circ, 38.5^\circ, 50.1^\circ$ , and  $59.8^\circ$  (ICDD file no. 37-1484) indicates that  $ZrO_2$  is dispersed on  $TiO_2$  and  $TiO_2-CeO_2$  supports.<sup>30</sup>

In addition, the absence of crystalline features of  $V_2O_5$  in the case of the vanadia based materials indicates that vanadium oxide is also dispersed on the surface of the support as vanadates or under the form of small vanadia crystallites undetectable *via* XRD.<sup>31</sup>

### 3.4 X-ray photoelectron spectroscopy

To investigate the surface composition of the catalysts, XPS measurements were performed. The electron binding energies

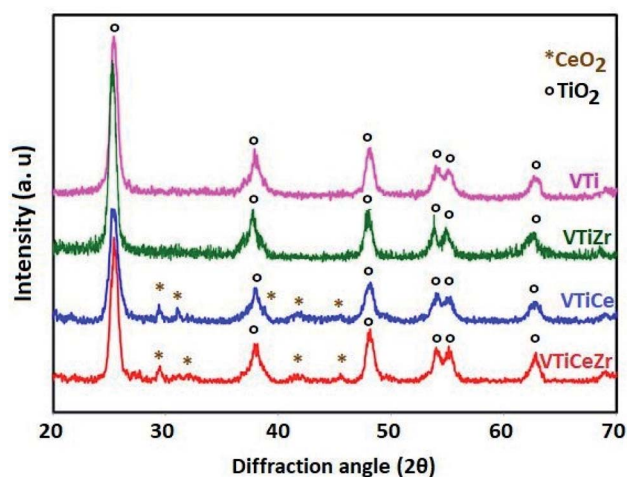


Fig. 3 X-ray diffraction patterns of  $V_2O_5$  based catalysts calcined at 500 °C.

(eV) of Ti 2p, Ce 3d, Zr 3d and V 2p and the surface atomic ratios V/Ti, V/(Ti + Zr), V/(Ti + Ce), V/(Ti + Ce + Zr) are displayed in Table 3.

Table 3 reveals that vanadia spreads more on the surface of  $TiO_2$  and  $TiO_2-CeO_2$  aerogel supports in the absence of zirconium since ratios (V/Ti and V/(Ti + Ce)) diminish when zirconia was incorporated.

The XPS spectra of Ti, Zr, O, Ce and V are presented in Fig. 4. The binding energies of Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> were found around 459 and 464 eV for all catalysts. These mentioned results were illustrated in Fig. 4(a). A contribution with binding energies around 182 and 184 eV was detected for samples containing zirconia (Fig. 4(b)). These peaks concerned Zr 3d<sub>3/2</sub> and Zr 3d<sub>5/2</sub>. Both Ti 2p and Zr 3d binding energies revealed the presence of 4+ oxidation state for Zr and Ti in the prepared samples.<sup>30,32</sup> However, no indication was observed for metallic Zr (~178 eV).<sup>32</sup>

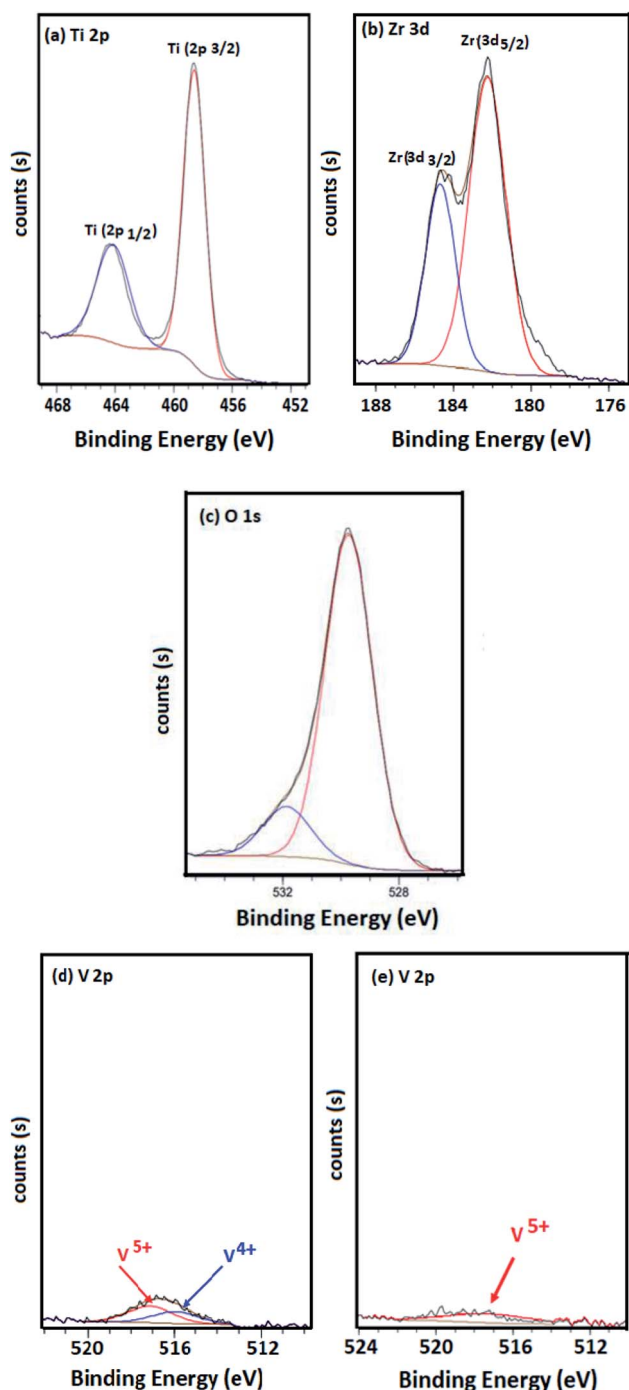
The spectra of O 1s for the four catalysts were investigated (Fig. 4(c)) and the results showed a main peak located at 530 eV which is typically assigned to the lattice oxygen associated to the metal oxides.<sup>33,34</sup>

Moreover, in the absence of zirconium, a contribution with binding energies around 515 and 517 eV is detected for VTi and VTiCe samples, suggesting that vanadium is a mixture of IV and V oxidation states (Fig. 4(d)).<sup>35</sup> However, doping catalysts with zirconium induces a higher oxidation state of vanadium since only binding energy of  $V^{5+}$  is detected (Fig. 4(e)). This result is very promising for the reactivity of  $V_2O_5$  based catalysts in the total oxidation of chlorobenzene since the catalytic response is strongly governed by the higher vanadium oxidation level.<sup>36</sup>

The Ce 3d XPS profiles of VTiCe and VTiZrCe samples treated at 500 °C are shown in Fig. 5. The two samples exhibit peaks due to the presence of both  $Ce^{4+}$  and  $Ce^{3+}$ , implying that cerium is present at the surface in both 4+ and 3+ oxidation states.<sup>37,38</sup> In particular, the sub-bands labeled with u''', u'', u, v''', v'' and v represent the 3d<sup>10</sup>4f<sup>0</sup> state of  $Ce^{4+}$ ,<sup>39</sup> and the sub-bands labeled

**Table 3** XPS Binding energies and V/X (X = Ti, Ti + Ce, Ti + Zr + Ce) atomic ratios of the VTi, VTiCe, VTiZr and VTiCeZr catalysts calcined at 500 °C

Catalyst	Binding energy (eV)						Atomic ratio V/X (X = Ti, Ti + Zr, Ti + Ce, Ti + Zr + Ce)			
	Ti 2p <sub>3/2</sub>	Ce 3d <sub>5/2</sub>	Zr 3d <sub>3/2</sub>	Zr 3d <sub>5/2</sub>	V <sup>5+</sup> 2p <sub>3/2</sub>	V <sup>4+</sup> 2p <sub>3/2</sub>	V/Ti	V/(Ti + Zr)	V/(Ti + Ce)	V/(Ti + Ce + Zr)
VTi	458.2	—	—	—	517.2	515.9	0.032	—	—	—
VTiCe	458.5	884.5	—	—	517.3	515.7	—	—	0.077	—
VTiZr	485.3	—	182.0	184.6	517.3	—	—	0.019	—	—
VTiZrCe	485.2	—	182.2	184.4	517.3	—	—	—	—	0.047

**Fig. 4** XPS spectra of elements: (a) Ti, (b) Zr, (c) O, (d) and (e) V.

with  $u$ ,  $u^\circ$ ,  $v$  and  $v^\circ$  represent the  $3d^9 4f^1$  state corresponding to  $Ce^{3+}$ .<sup>39</sup> However, the calculated  $Ce^{3+}$  fraction of zirconia containing catalyst (61%) is higher than that of VTiCe (37%), indicating that the catalyst with added  $ZrO_2$  contains more  $Ce^{3+}$  ions that provides more redox active sites on catalyst surface and plays the role of oxygen vacancy. This result is very promising for the chlorobenzene abatement which is related to the enhanced redox properties.

### 3.5 $NH_3$ -TPD

To evaluate the acidic properties of the elaborated oxides,  $NH_3$ -TPD experiments were undertaken. The obtained profiles are displayed in Fig. 6. The  $NH_3$  desorption profile of VTi shows two unresolved peaks at around 100 °C and 350 °C which are attributed, respectively, to weak and strongly adsorbed ammonia (Fig. 6(a)).<sup>1,40,41</sup> The incorporation of this sample enhances the total acidity of this catalyst as proven by the increase of the intensities of the two peaks mentioned above<sup>8</sup>

Besides, it seems that the global acidity of  $V_2O_5/TiO_2$  and  $V_2O_5/TiO_2-CeO_2$  materials is influenced by the addition of  $ZrO_2$ . In particular, the intensity of the first peak centred at 100 °C increases considerably indicating that zirconium generates a new type of weak acid sites on the surface of  $V_2O_5/TiO_2$  catalyst which could reveal highly beneficial for the catalytic performances of  $V_2O_5/TiO_2$  as discussed in earlier works.<sup>1,42</sup> For VTiCeZr sample, the  $NH_3$ -desorption temperatures from weak acid sites are shifted toward higher temperatures reflecting an increase in the strength of the weak acid sites. This result is very promising since the acidity is crucial in the adsorption of the VOCs on its surface.<sup>1</sup>

Furthermore, the introduction of  $ZrO_2$  did not seem to change significantly the peak intensities of strong acidic sites in the case of VTiZr and VTiCeZr materials. However, TPD profile of  $V_2O_5/TiO_2-CeO_2-ZrO_2$  revealed that the strength of strong acid sites was higher than that of  $V_2O_5/TiO_2-CeO_2$  since the  $NH_3$ -desorption temperatures shifted toward higher temperatures. Based on literature,<sup>43</sup> strong acid sites which are present on the surface of supports improve the spreading of  $VO_x$  active phase and consequently, could favour a better catalytic activity.

### 3.6 $H_2$ -TPR

The reducibility of zirconium, vanadium and cerium species was examined by  $H_2$ -TPR (Fig. 7). The TPR profiles of  $V_2O_5$  based materials exhibit unresolved peaks maximizing at about 491 °C, 474 °C and 441 °C which might be ascribed to the reduction of



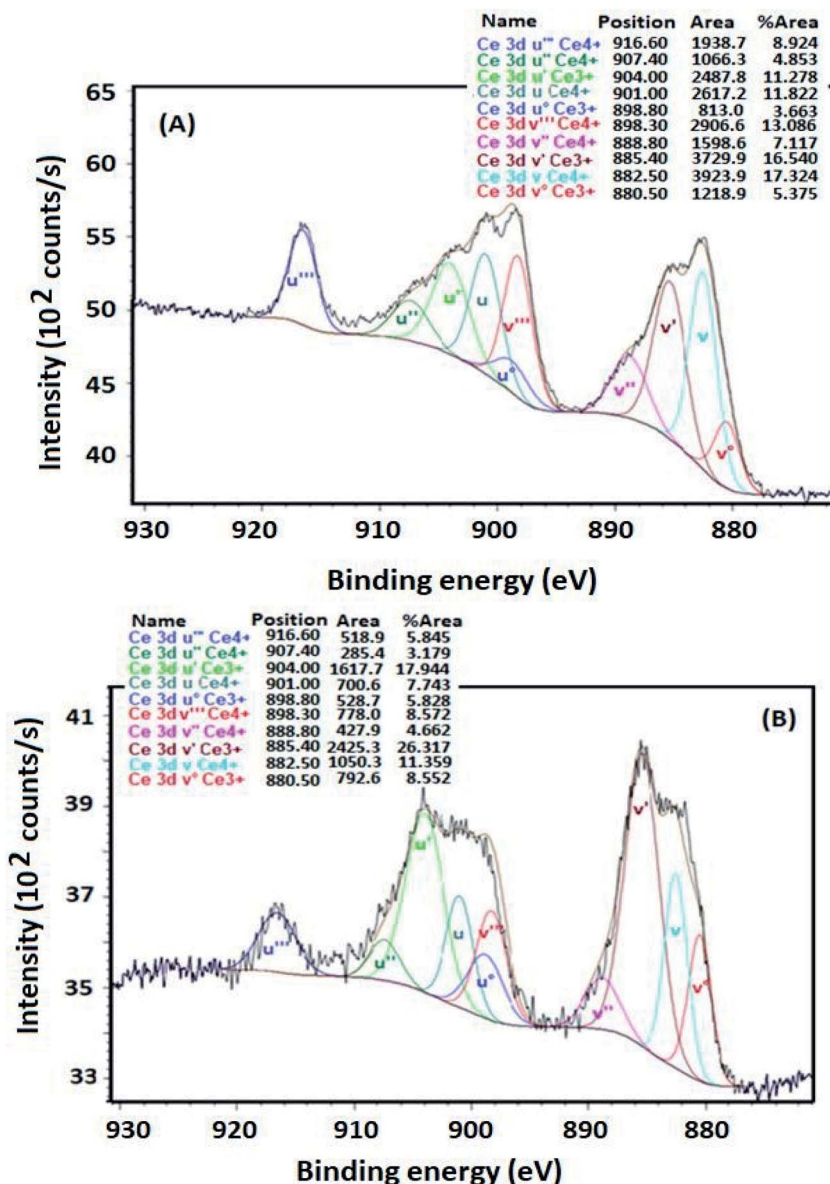


Fig. 5 Ce 3d XPS profile of samples treated at 500 °C, (A) Ce 3d XPS profile of VTiCe catalyst, (B) Ce 3d XPS profile of VTiCeZr catalyst.

dispersed  $\text{VO}_x$  species.<sup>44,45</sup> It is clear that the incorporation of zirconium affects the reduction behavior of vanadium species. Especially, the reducibility of vanadium becomes more important in the VTiCeZr solid than that of VTi and VTiZr materials since TPR reduction peaks shifted toward lower temperature. These observations suggest that the presence of zirconium species enhance the reduction ability of catalysts. Thus, the VTiCeZr material with better reducibility could indicate better oxygen absorbing capacity and hence could lead to a better catalytic performances.

After ceria addition, a new peak centered at 548 °C appeared in the TPR profile of the  $\text{V}_2\text{O}_5/\text{TiO}_2\text{-CeO}_2$  which can be attributed to the reduction of surface  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ .<sup>46</sup>

For  $\text{ZrO}_2$  containing materials, peaks revealed at 584 °C and 578° for VTiZr and VTiCeZr respectively, could be attributed to the reduction of  $\text{ZrO}_2$ .<sup>47</sup>

The TPR profile of VTiCeZr catalyst exhibits two peaks around 638 °C and 692 °C which are attributed to the reduction of bulk  $\text{CeO}_2$ .<sup>48,49</sup> The reduction temperatures are lower than that of  $\text{CeO}_2$  (above 700 °C<sup>49,50</sup>). This was associated with the  $\text{ZrO}_2$  ability to modify sublattice oxygen into  $\text{CeO}_2\text{-ZrO}_2$  mixed oxides, generating defective structures and highly mobile oxygen atoms.<sup>49,51</sup>

Combined with the XPS results, the good reducibility owing to the increase of the amount and the kinds of reactive oxygen species can provide a facile redox process that could contribute to enhancing the catalytic activity.

### 3.7 Catalytic test

The catalytic investigation was performed in the total oxidation of chlorobenzene in order to probe the ability of the prepared





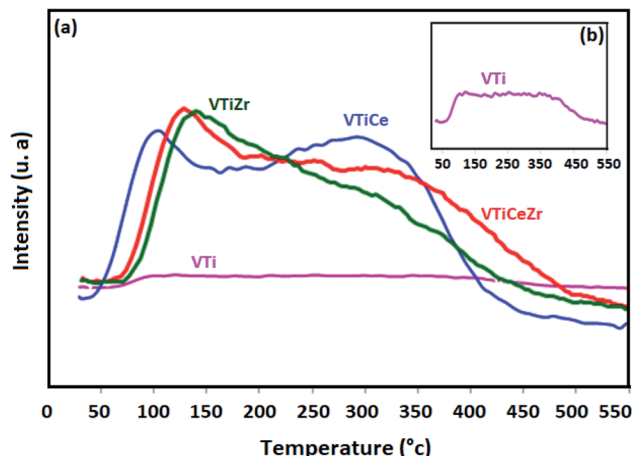


Fig. 6  $\text{NH}_3$ -TPD profiles of catalysts treated at 500 °C: (a)  $\text{NH}_3$ -TPD of VTi, VTiCe, VTiZr and VTiCeZr, (b)  $\text{NH}_3$ -TPD of VTi.

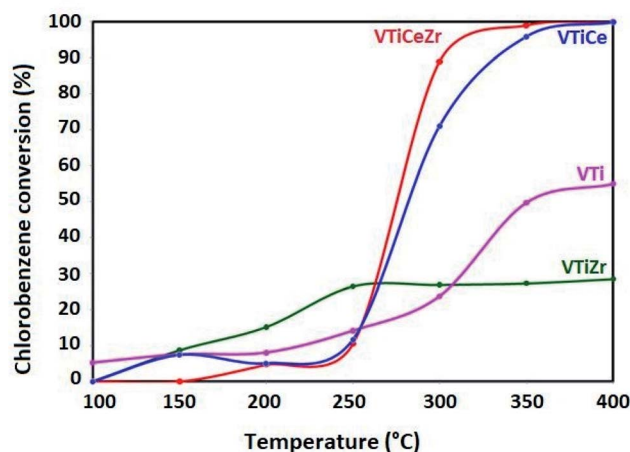


Fig. 8 Chlorobenzene conversion over vanadia supported catalysts.

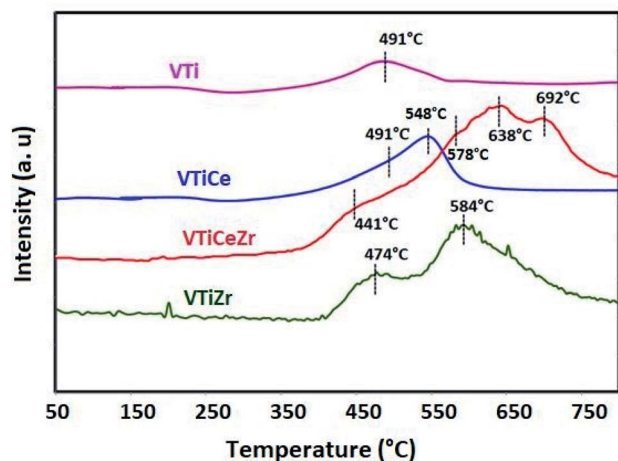


Fig. 7  $\text{H}_2$ -TPR profiles of VTi, VTiCe, VTiZr and VTiCeZr samples treated at 500 °C.

catalysts to convert chlorobenzene without deactivation. Fig. 8 presents the chlorobenzene light-off curves of the impregnated catalysts supported on  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-CeO}_2$ ,  $\text{TiO}_2\text{-ZrO}_2$  and  $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$  in the range 100–400 °C by steps of 50 °C. The reaction was run from 100 °C to 400 °C by steps of 50 °C. At each temperature investigated, the catalyst was stabilized for 150 min in order to reach the steady state.  $\text{CO}_2$  is the main product. The carbon balance is completed with carbon monoxide, which is also produced especially at a relatively high temperature (from a few % up to ca. 30%). No other partial oxidation products (chlorinated or not) are observed. These observations hold for all the catalysts.

The VTi reference catalyst is almost inactive up to 250 °C. However, it exhibits moderate activity above 300 °C and merely reaches 55% at 400 °C. The incorporation of zirconia into this catalyst brings a slight improvement in catalytic activity in the range (100–250 °C). This improvement could be attributed to (i) the better acidic properties, as shown by  $\text{NH}_3$ -TPD results, which help the adsorption of the pollutant and/or (ii) the

stabilization of the  $\text{V}_2\text{O}_5$  active phase in a higher oxidation state, as demonstrated by XPS results. Moreover, the superior activity of the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst in the range (300–400 °C) could be related to the higher V surface concentration in VTi sample than that shown by VTiZr as demonstrated by XPS results.

On the other hand, the  $\text{V}_2\text{O}_5\text{-TiO}_2\text{-CeO}_2$  and  $\text{V}_2\text{O}_5\text{-TiO}_2\text{-CeO}_2\text{-ZrO}_2$  catalysts hardly convert chlorobenzene below 250 °C and their activities increase with temperature to reach 100% conversion at 400 °C. However, their behavior with the increase of temperature is quite different. Especially, at 300 °C VTiCeZr catalyst converts 89% while VTiCe converts 71%. This observation pointed up the beneficial effect of the introduction of zirconium groups into the binary oxide  $\text{TiO}_2\text{-CeO}_2$  aerogel support. In particular, according to XPS results, it seems that zirconia succeeds to stabilize vanadium at a higher oxidation state ( $\text{V}^{5+}$ ). In fact, in the case of VTiCeZr catalyst, ceria mainly exists in the form of  $\text{Ce}^{3+}$ . The enrichment of  $\text{Ce}^{3+}$  could create a charge imbalance, and more oxygen vacancies are formed. This could facilitate the activation and transportation of active oxygen species. Indeed,  $\text{CeO}_2$  is a powerful oxidant for the regeneration of the  $\text{V}_2\text{O}_5$  reduced sites. This higher oxidation strength of  $\text{CeO}_2$  assisted by  $\text{ZrO}_2$  induces a speeding up of the Mars and van Krevelen mechanism.<sup>52</sup> This speeding up corresponds to the observed increase of the chlorobenzene conversion. This result correlates well with that obtained by  $\text{H}_2$ -TPR. Particularly, VTiCeZr catalyst with better reducibility is the most active catalyst.

## 4. Conclusion

Our results revealed that Zr-doped  $\text{V}_2\text{O}_5$  based catalyst is beneficial for the improvement of catalytic properties in chlorobenzene total oxidation. In particular, in the absence of cerium groups, this beneficial effect is in the range (100–250 °C) and it is essentially correlated with the better acidic properties or/and the stabilization of the  $\text{V}_2\text{O}_5$  active phase in a higher oxidation state. However, in the case of cerium rich catalyst, this positive effect is much stronger. In fact,  $\text{ZrO}_2$  increases the



oxygen mobility in the lattice, which, in turn, enhances the redox properties of  $\text{V}_2\text{O}_5/\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$  and induces an increase in the chlorobenzene conversion, especially from 300 °C.

## Conflicts of interest

There are no conflicts to declare.

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