

# Spectroscopic characterization of vanadium(v) oxo species deposited on zirconia

Margarita Kantcheva

Department of Chemistry, Faculty of Science, Bilkent University, 06533 Bilkent, Ankara, Turkey.  
E-mail: margi@fen.bilkent.edu.tr

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A method for deposition of vanadium(v) oxo species from acidic solutions of ammonium metavanadate on zirconia is described. The samples are synthesized by suspension of the support (powder) in solutions containing three different vanadium(v) precursor ions: the dioxovanadium(v) ion,  $\text{VO}_2^+$ , the yellow diperoxo anion  $[\text{VO}(\text{O}-\text{O})_2]^-$  and the red monoperoxo cation  $[\text{VO}(\text{O}-\text{O})]^+$ . Application of vanadium(v) peroxo complexes increases significantly the uptake of vanadium by zirconia. The state and localization of the  $\text{VO}_x$  species on the surface of zirconia were studied by FTIR, UV/VIS and XP spectroscopies. The materials prepared from  $\text{VO}_2^+$  ions contain isolated  $\text{VO}_4$  groups and domains of orthovanadate species,  $(\text{VO}_4)_n$ . The FTIR spectra of adsorbed CO revealed that the number of exposed  $\text{Zr}^{4+}$  ions decreased markedly when vanadium(v) peroxo ions were used as precursors. The predominant surface structure in this case was identified as pyrovanadates,  $\text{V}_2\text{O}_7$ . On all of the samples studied no separate phase of  $\text{V}_2\text{O}_5$  was detected.

## Introduction

Supported vanadia catalysts are extremely effective in the processes of selective oxidation of various hydrocarbons and selective catalytic reduction of  $\text{NO}_x$ .<sup>1–7</sup> The most widely used support in these catalysts is the low-temperature modification of titanium dioxide, anatase. However, this form of titania has a relatively low specific surface area and low thermal stability. Therefore, zirconium dioxide has attracted attention as an alternative support by taking advantage of its high thermal stability.<sup>8</sup> The structural and physico-chemical characteristics of  $\text{VO}_x/\text{ZrO}_2$  catalysts have been reported in several papers.<sup>5,9–15</sup> Sohn *et al.*<sup>9</sup> showed that the interaction between vanadium(v) oxide and zirconia has an anti-sintering effect and the catalysts possess high specific surface areas up to 873 K. Ghiotti *et al.*<sup>10,11</sup> concluded that the nature of the vanadate species on the surface of zirconia is determined mainly by the vanadium content and does not depend on the conditions of preparation. Investigations have shown that vanadia-zirconia catalysts possess good activity and selectivity in the SCR of  $\text{NO}_x$ .<sup>11,14,16</sup> and their performance depends on the amount of specific polyvanadates.<sup>11,16</sup>

It was demonstrated<sup>17–19</sup> that the capacity of  $\text{TiO}_2$  (anatase) for adsorption of vanadium(v) oxo species from acidic solutions increases after pre-treatment of the support with hydrogen peroxide. This results in a more homogeneous distribution of the active phase and to the absence of exposed  $\text{Ti}^{4+}$  cations on the catalyst surface. Vanadium(v) and zirconium(iv) form peroxo complexes when dissolved in solutions of hydrogen peroxide.<sup>20,21</sup> It is of interest to study the possibility of application of peroxovanadium(v) ions as precursors of  $\text{VO}_x/\text{ZrO}_2$  catalysts. In this paper, solid materials obtained by adsorption from aqueous solutions containing dioxovanadium(v) ions and peroxovanadates were characterized by various spectroscopic methods (FTIR, UV/VIS spectroscopy, XPS and FTIR spectroscopy of adsorbed CO) in order to specify the nature of the  $\text{VO}_x$  species and their localization on the surface of zirconia.

## Experimental

### 1. Synthesis of the $\text{VO}_x/\text{ZrO}_2$ samples

The zirconia support was prepared by hydrolysis of  $\text{ZrCl}_4$  with a concentrated (25%) solution of ammonia. After drying, the precipitate was calcined for 4 h at 773 K. According to XRD the substance has a monoclinic structure.

The  $\text{VO}_x/\text{ZrO}_2$  samples were obtained by adsorption from aqueous solutions of ammonium metavanadate (0.06 mol  $\text{dm}^{-3}$ ) containing three different vanadium(v) oxo species:

- The  $\text{VO}_2^+$  ion. The solution of this species (indicated as solution 1) was prepared by dissolving ammonium metavanadate in dilute nitric acid (1 : 4) at pH 0.5;
- The yellow diperoxo anion  $[\text{VO}(\text{O}-\text{O})_2]^-$ . This species was obtained by dissolving ammonium metavanadate in 5%  $\text{H}_2\text{O}_2$  at pH 4.5 (solution 2); and
- The red monoperoxo cation  $[\text{VO}(\text{O}-\text{O})]^+$  was prepared by acidification of solution 2 with dilute nitric acid to pH 0.5 (solution 3).

The conditions for existence of these ions are described in ref. 20.

The zirconia support (5 g) was suspended in the corresponding solution (100  $\text{cm}^3$ ) for a given time under constant stirring at room temperature. Then, the precipitate was filtered, washed several times with de-ionized water, dried in air at 383 K and calcined for 2 h at 723 K. The materials obtained in this way are denoted by  $x\text{VZy}$ , where  $x$  stands for the time of adsorption (2 or 24 h) and  $y$  indicates the solution containing the corresponding precursor vanadium(v) oxo ion.

### 2. Methods

The UV/VIS absorption spectra were measured with a Cary 5E UV/VIS/NIR spectrometer. The reference substance was either hydrated or dehydrated zirconia [calcined in three cycles for 1 h at 673 K in dry oxygen (13.3 kPa) and then cooled to room temperature in the same atmosphere].

The XP spectra were taken with a KRATOS ES300 spectrometer with a non-monochromatized Mg K $\alpha$  radiation source (120 W). Samples in the form of pressed pellets were prepared *ex situ* and introduced into the vacuum chamber ( $<1.33 \times 10^{-5}$  kPa). Quantification was done using the areas of the V<sub>2p 3/2</sub> and Zr<sub>3d 5/2</sub> peaks after linear background subtraction and correction for the photoionization, cross-section and instrumental factors. The curve-fitting was done by a least-squares method using a mixed Gaussian–Lorentzian function. The binding energy of O<sub>1s</sub> was taken as a reference.

The FTIR spectra were recorded on a Bomem MB 102 FTIR (Hartman & Braun) spectrometer at a resolution of 4 cm<sup>-1</sup> (512 scans). A specially designed IR cell allowed registration of the spectra at ambient temperature and sample activation at higher temperatures. The cell was connected to a vacuum/adsorption apparatus. Self-supporting discs were used for the FTIR studies.

Before the absorption measurements, the samples pressed in thin pellets (0.030 g cm<sup>-2</sup>) were activated by heating for 1 h *in vacuo* at 673 K and in oxygen (13.3 kPa) at the same temperature followed by evacuation for 1 h at room temperature.

The BET surface areas were measured by nitrogen adsorption at 77 K using a MONOSORP apparatus from Quantochrome (USA).

The vanadium content was determined spectrophotometrically by measuring the absorbance of acidic solutions of V<sup>5+</sup> ions in 0.03% H<sub>2</sub>O<sub>2</sub>.<sup>22</sup>

### 3. Reagents

All the reagents used were of analytical-reagent grade. The carbon monoxide (99.95%) was passed through a trap cooled in liquid nitrogen before admission to the IR cell.

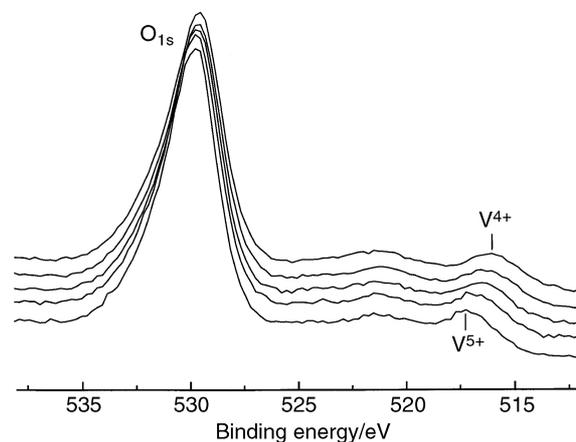
## Results

### 1. Surface vanadium concentration

According to the data of the chemical analysis and XPS (Table 1) the highest coverage by vanadium is obtained when the adsorption of VO<sub>x</sub> species on zirconia is performed in solution 3 (containing the monoperoxo cation [VO(O–O)]<sup>+</sup>). The calculated vanadium uptake from chemical analysis corresponds to 5.1 V<sup>5+</sup> nm<sup>-2</sup>. According to XPS, the V : Zr ratio for the samples 24VZ2 and 24VZ3 is higher than that determined by chemical analysis and is indicative of surface localization of the VO<sub>x</sub> species. The ratio for the 2VZ1 and 24VZ1 samples is uncertain due to the low intensity of the V<sub>2p 3/2</sub> peak in the XP spectrum. The number of theoretical monolayers was calculated from the V<sup>5+</sup> loading, the surface area of the support and the estimated area occupied by the VO<sub>2.5</sub> unit ( $1.05 \times 10^{-19}$  m<sup>2</sup>).<sup>14</sup>

### 2. Oxidation state of vanadium in the surface VO<sub>x</sub> species

The XP spectrum of the sample 24VZ3 is presented in Fig. 1. The oxygen 1s peak occurs at 530 eV. The peak of V<sub>2p 3/2</sub> observed after the first 10–30 scans is positioned at 517 eV



**Fig. 1** Development of XP spectrum of sample 24VZ3 with the increase in time of exposure to X-rays.

and shifts to 516 eV as the time of X-ray exposure increases. The former peak is assigned to vanadium in oxidation state +5 whereas the latter is attributed to vanadium(IV).<sup>12,18,19</sup> These results show that during the XPS characterization of the sample a reduction of vanadium(v) to vanadium(IV) occurs. The other materials show the same behavior. From these data it is concluded that the samples contain originally vanadium in the +5 oxidation state.

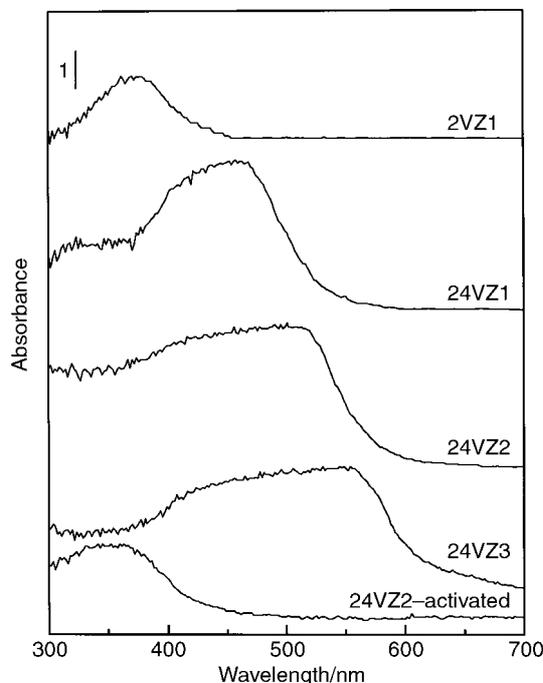
### 3. Coordination number of vanadium(V) in the surface VO<sub>x</sub> species

The absorption spectrum of ZrO<sub>2</sub> (not shown) is characterized by two strong bands at 208 and 228 nm and a weak band at about 280 nm.

The spectra of the samples investigated in the visible range, taken under ambient conditions, are shown in Fig. 2. In the same figure, the spectrum of the sample 24VZ2 recorded immediately after the activation in the IR cell is also presented. For all of the samples of the series 24VZY exposed to ambient conditions a broad, unresolved absorption between 400 and 550 nm is observed. The position of the absorption maxima is strongly influenced by the vanadium content—an increase in the vanadium coverage causes a noticeable red shift. This accounts for the occurrence of progressive oligomerization through formation of V–O–V linkages leading to agglomeration of the immobilized VO<sub>x</sub> species.<sup>23–26</sup> The spectrum of the activated 24VZ2 sample exhibits a completely different pattern. It has a broad unresolved band at 325–375 nm and is more similar to the spectrum of the 2VZ1 sample characterized by the lowest VO<sub>x</sub> coverage. The differences in the spectra between the dehydrated (activated) and hydrated (exposed to ambient conditions) 24VZ2 sample can be explained by the tendency of coordinatively unsaturated VO<sub>x</sub> species to complete their coordination sphere by adding water<sup>25–27</sup> or other molecules<sup>27</sup> as ligands. Indeed, V<sup>5+</sup> ions in an octahedral environment give a charge-transfer band (O → V<sup>5+</sup>) at 450–550 nm, while five-coordinated

**Table 1** Physico-chemical characteristics of the samples investigated

Sample	Precursor ion	V <sup>5+</sup> loading (wt.-%)	S /m <sup>2</sup> g <sup>-1</sup>	Surface ratio V : Zr (XPS)	Surface concentration /V <sub>5+</sub> nm <sup>-2</sup> (from chemical analysis)	Number of theoretical monolayers of V <sub>2</sub> O <sub>5</sub> on ZrO <sub>2</sub>
ZrO <sub>2</sub>	—	—	69	—	—	—
2VZ1	VO <sub>2</sub> <sup>+</sup> , pH 0.5	0.6	75	—	1.0	0.1
24VZ1	VO <sub>2</sub> <sup>+</sup> , pH 0.5	1.3	90	(1.1 : 100)	2.2	0.2
24VZ2	[VO(O–O) <sub>2</sub> ] <sup>-</sup> , pH 4.5	2.2	167	5.8 : 100	3.8	0.4
24VZ3	[VO(O–O)] <sup>+</sup> , pH 0.5	3.0	91	9.6 : 100	5.1	0.5

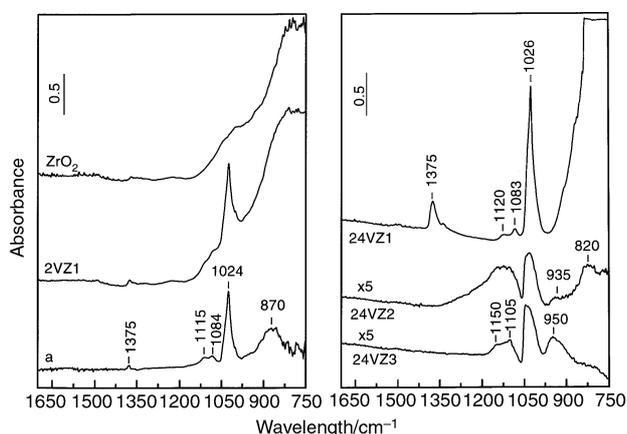


**Fig. 2** Absorption spectra in the visible range of the samples studied exposed to ambient conditions and of sample 24VZ2 immediately after activation.

vanadium(v) is characterized by an absorption at 400–415 nm.<sup>19,23–26,28</sup> The absorption at 325–375 nm, associated with the 2VZ1 and dehydrated 24VZ3 samples, is typical for four-coordinated vanadium(v)<sup>19,23–26,28</sup> in pseudo-tetrahedral geometry.<sup>26</sup> It should be pointed out that the coordination number of vanadium(v) in the hydrated 2VZ1 sample is not influenced by the adsorbed water as with the 24VZ2 sample. This indicates that the surface tetrahedral vanadium(v) species are isolated and no oligomerization, probably, through water bridges takes place.

#### 4. FTIR spectroscopy of the activated samples

**4.1. FTIR spectra in the  $\nu(\text{V-O})$  fundamental and “first overtone” region.** In order to identify the surface  $\text{VO}_x$  species, *in situ* FTIR spectra of the activated samples were taken in the  $\nu(\text{V-O})$  fundamental and “first overtone” region. The spectra of the  $\text{ZrO}_2$  support and the 2VZ1 sample in the 1700–750  $\text{cm}^{-1}$  region are shown in Fig. 3. No residual carbonate groups (which may be present on the surface of zirconia after



**Fig. 3** FTIR spectra of the samples studied in the fundamental V–O stretching region. The spectra (a), 24VZ2 and 24VZ3 are obtained by subtraction of the spectrum of  $\text{ZrO}_2$  from the full spectra of the samples 2VZ1, 24VZ2 and 24VZ3, respectively.

the activation procedure) are detected. In the same figure the subtraction spectrum (the spectrum of sample 2VZ1 minus the spectrum of zirconia) is also presented. The resulting spectrum exhibits weak bands at 1375, 1335, 1115 and 1084  $\text{cm}^{-1}$ , a strong and asymmetric band with a maximum at 1024  $\text{cm}^{-1}$  and a wide and complex absorption between 925 and 800  $\text{cm}^{-1}$ . The sharp band with a maximum at 1024  $\text{cm}^{-1}$  is attributed to the fundamental V=O stretching mode of surface  $\text{VO}_x$  species (see Discussion). The increase in the time of adsorption of the precursor cation  $\text{VO}_2^+$  on the surface of zirconia (sample 24VZ1) leads to doubling of the vanadium(v) loading (Table 1). This causes a strong increase in the intensity of the band at 1024  $\text{cm}^{-1}$  (now shifted to 1026  $\text{cm}^{-1}$ ) and that of the doublet at 1375 and 1335  $\text{cm}^{-1}$  (Fig. 3). The intensity increase of the latter two bands is stronger than that of the former. This suggests that the origin of these bands is different. The absorption below 1000  $\text{cm}^{-1}$  became very strong which makes the subtraction of the spectrum of the support impossible. However, shoulders at about 910 and 860  $\text{cm}^{-1}$  can be visualized. The intensity of the band at 1115  $\text{cm}^{-1}$  (shifted to 1120  $\text{cm}^{-1}$ ) has decreased slightly whereas that of the band at 1083  $\text{cm}^{-1}$  is almost unchanged.

The change of the precursor to peroxo ions results in a further increase in the vanadium(v) loading (Table 1). This is accompanied by disappearance of the band at 1026  $\text{cm}^{-1}$  and an unresolved and much weaker absorption between 1050 and 1000  $\text{cm}^{-1}$  is detected instead (Fig. 3). It can be attributed to V=O stretching modes of surface  $\text{VO}_x$  species with increased nuclearity. The absorption in the 1200–1050  $\text{cm}^{-1}$  region became broader. The bands in the 1050–1000  $\text{cm}^{-1}$  region display a blue shift on increasing the vanadium content. The doublet at 1375 and 1335  $\text{cm}^{-1}$  is not present and the strong absorption below 1000  $\text{cm}^{-1}$ , observed for the 24VZ1 sample, disappeared. The spectrum of sample 24VZ2 exhibits also a weak band at about 935  $\text{cm}^{-1}$  and unresolved absorption between 850 and 790  $\text{cm}^{-1}$ . For the 24VZ3 sample, the latter absorption has almost disappeared, the band at 935  $\text{cm}^{-1}$  has grown and its maximum is positioned at 950  $\text{cm}^{-1}$ .

In brief, the spectra in the 1400–800  $\text{cm}^{-1}$  region of the materials prepared from peroxo ions (24VZ2 and 24VZ3) display similar features and differ considerably from those of the samples obtained from the  $\text{VO}_2^+$  cation (2VZ1 and 24VZ1). This suggests that different kinds of surface  $\text{VO}_x$  species are formed on the surface of zirconia depending on the type of precursor ion used. Further evidence for this conclusion comes from the spectra of the samples studied, taken in the first V=O overtone region (Fig. 4). For  $x\text{VZ1}$  samples, the increase in the vanadium loading due to the longer time of the adsorption of the precursor  $\text{VO}_2^+$  cation (sample 24VZ1), causes a proportional increase in the intensities of the V=O fundamental and overtone bands. However, despite the substantial drop in the intensities of the fundamental V=O band after the change of the precursor ion, the intensities of the overtone bands for samples 24VZ2 and 24VZ3 are comparable to that of 24VZ1 (compare Fig. 3 and 4). This experimental fact confirms the conclusion that two different kinds of surface  $\text{VO}_x$  species are deposited on zirconia depending on whether dioxo or peroxo vanadium(v) ions are used as precursors.

**4.2. FTIR spectra in the OH stretching region.** The FTIR spectra in the OH stretching region of the solid materials studied are shown in Fig. 5A. The spectrum of the  $\text{ZrO}_2$  support is characterized by absorption at 3750, 3660, 3400 and 3265  $\text{cm}^{-1}$ . According to the literature data<sup>29–31</sup> these bands are assigned to terminal hydroxyls (3750  $\text{cm}^{-1}$ ) and bridged OH groups coordinated to two (3660  $\text{cm}^{-1}$ ) and three Zr atoms (3400  $\text{cm}^{-1}$ ). The absorption at 3265  $\text{cm}^{-1}$  is attributed to H-bonded OH groups. The sample 24VZ1 prepared from the dioxovanadium(v) cation displays a spectrum similar

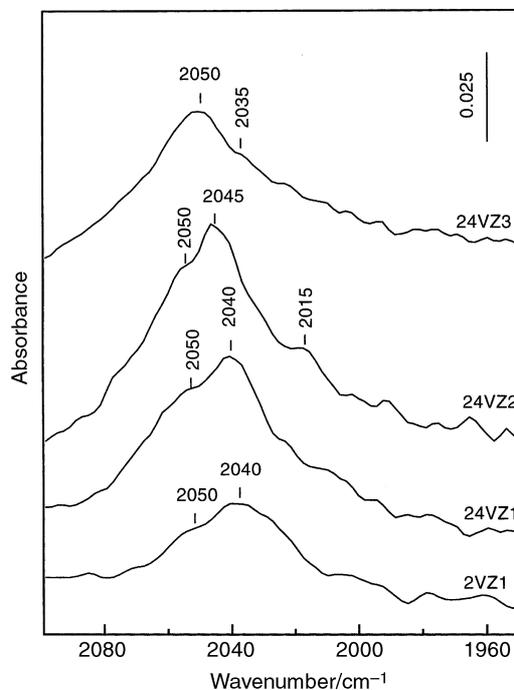


Fig. 4 FTIR spectra of the samples studied in the  $2\nu(\text{V}=\text{O})$  region.

to that of zirconia with narrower bands. The intensities of the three-coordinated OH groups of the support are reduced relative to the two-coordinated hydroxys. This is evidence for the participation of the former hydroxy groups in the deposition of vanadium(v). For samples 24VZ2 and 24VZ3 the total population of the surface OH groups of zirconia is reduced. However, during the adsorption of peroxovanadium(v) ions, the terminal and two-coordinated hydroxys are affected to a much larger extent than the three-coordinated ones.

It seems that surface OH groups of the type  $\text{V}^{5+}-\text{OH}$  are not formed. The latter are characterized by absorption at  $3660\text{ cm}^{-1}$ .<sup>17–19</sup> However, the absorption in this region decreases with an increase in the vanadium loading.

### 5. Surface characterization by FTIR spectroscopy of adsorbed CO

The adsorption of CO (4 kPa) at room temperature on the  $\text{ZrO}_2$  sample leads to the appearance of two bands with maxima at  $2196$  and  $2189\text{ cm}^{-1}$  (Fig. 5B). In accordance with the literature,<sup>32</sup> they correspond to C–O stretching modes of two kinds of  $\text{Zr}^{4+}-\text{CO}$  surface carbonyls, high- $[(\text{CO})_{\text{H}}]$  and low-frequency  $[(\text{CO})_{\text{L}}]$  species, respectively.

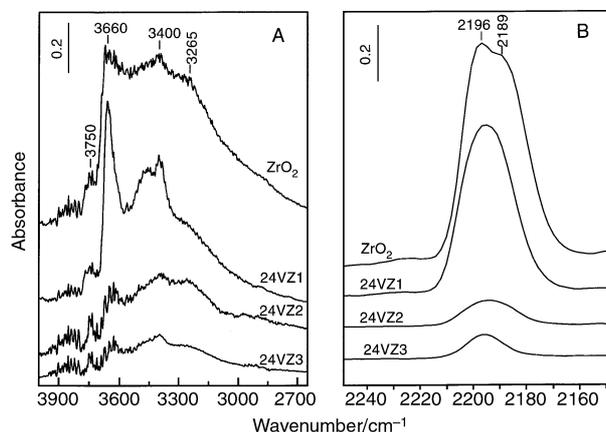


Fig. 5 A: FTIR spectra of the activated samples in the hydroxy region. B: FTIR spectra of adsorbed CO (4 kPa) at 298 K on the activated samples.

The spectrum of CO adsorbed on sample 24VZ1 prepared from  $\text{VO}_2^+$  ions shows the presence of a band at  $2196\text{ cm}^{-1}$ , assigned to the  $(\text{CO})_{\text{H}}$  species of zirconia (Fig. 5B). Since CO does not form carbonyls with  $\text{V}^{5+}$  ions,<sup>17–19,24,33,34</sup> this experimental fact indicates that mainly the  $(\text{CO})_{\text{L}}$  sites of the support are blocked by the  $\text{VO}_x$  species.

The adsorption of CO on samples 24VZ2 and 24VZ3 reveals that the number of exposed  $\text{Zr}^{4+}$  ions decreases markedly when peroxovanadium(v) ions are used as precursors. A considerable portion of the  $(\text{CO})_{\text{L}}$  and  $(\text{CO})_{\text{H}}$  sites are not accessible to CO adsorption. The extent of blocking the  $(\text{CO})_{\text{L}}$  sites is greatest for sample 24VZ3. These results indicate that the  $\text{VO}_x$  species on the surface of 24VZ2 and 24VZ3 samples are located in the vicinity of both Lewis acid sites of the support. All the spectra shown in Fig. 5B are normalized by factors accounting for the difference in the BET surface area at constant weight of the pellet.

## Discussion

### 1. Nature of the $\text{VO}_x$ species deposited on the surface of zirconia

The vanadium loading of all of the materials studied is lower than that corresponding to a theoretical monolayer. However, from the FTIR results, it is evident that not only isolated but also polymeric  $\text{VO}_x$  species are present on the surface of the zirconia.

For samples with coverage up to  $2\text{ V}^{5+}\text{ nm}^{-2}$  (2VZ1 and 24VZ1 prepared from solutions containing  $\text{VO}_2^+$ ) the band at  $1375\text{ cm}^{-1}$  with a shoulder at  $1335\text{ cm}^{-1}$  and the complex absorption in the region  $925\text{--}800\text{ cm}^{-1}$  (Fig. 3) grow with an increase in the vanadium content. Similar bands were reported by Busca *et al.*<sup>35</sup> in the IR spectrum of bulk magnesium orthovanadate,  $\text{Mg}_3(\text{VO}_4)_2$ . The detailed analysis of the IR data on this compound shows that the orthovanadate species are characterized by terminal V–O stretching modes responsible for a strong IR band at  $861\text{ cm}^{-1}$  with satellites at  $915$  and  $833\text{ cm}^{-1}$ . For this compound a strong band at  $1347\text{ cm}^{-1}$  is also observed which is assigned to a combination of the symmetric stretching of the  $\text{VO}_4^{3-}$  ion with a deformation mode. It can be concluded that  $(\text{VO}_4)_n$  clusters are formed on the surface of the samples of the  $x\text{VZ1}$  series characterized by the complex band with a maximum at  $870\text{--}860\text{ cm}^{-1}$  ( $\text{VO}_4$  stretching mode, observed for the 2VZ1 sample) and the combination bands at  $1375$  and  $1335\text{ cm}^{-1}$  (Fig. 3). The presence of two combination modes suggests that probably two types of  $(\text{VO}_4)_n$  clusters are formed differing in their location.

The assumption of  $(\text{VO}_4)_n$  cluster formation is supported by the UV/VIS data, which show the presence of tetrahedral  $\text{VO}_4$  species on sample 2VZ1. These surface forms, at low vanadium loading ( $1\text{ V}^{5+}\text{ nm}^{-2}$ ), do not tend to polymerize under moist conditions. On increase of the vanadium content to  $2\text{ V}^{5+}\text{ nm}^{-2}$ , the maximum of the absorption band shifts to higher wavelength which is associated with the increased number and size of the  $(\text{VO}_4)_n$  domains. The increased density of the  $\text{VO}_4$  species on the surface favors their polymerization through bridges of water molecules.

The sharp asymmetric band with a maximum at  $1026\text{--}1024\text{ cm}^{-1}$  observed on samples 2VZ1 and 24VZ1 can be attributed to surface V=O groups. This assignment agrees with the Raman and IR data on supported vanadium oxide materials previously reported.<sup>5,18,19,25,27,28,36–38</sup> The increase in the intensity of this band on increase in the vanadium loading (samples 2VZ1 and 24VZ1) is accompanied by a strong increase in the absorption below  $1000\text{ cm}^{-1}$  (see Fig. 3). A similar effect was observed by others<sup>10,11,16</sup> and was attributed to surface Zr–O–V stretching modes. This means that the band at  $1065\text{--}980\text{ cm}^{-1}$  contains contributing peaks from  $\nu(\text{V}=\text{O})$  stretching modes of isolated  $\text{VO}_4$  species directly

bonded to the support (in accordance with the tetrahedral coordination of the  $V^{5+}$  ions). The complex character of this absorption and its overtone reveal the existence of several kinds of  $VO_4$  species containing terminal V–O bonds differing in bond length and bond order, respectively. As shown by Lietti *et al.*<sup>38</sup> and Ramis *et al.*<sup>39</sup> the frequency of the  $\nu(V=O)$  stretching mode is influenced by the basicity of the oxygen ligands involved in the coordination sphere of the  $VO_x$  species. The increased basicity leads to a red shift in the position of the  $\nu(V=O)$  band which accounts for longer and weaker terminal V–O bonds. It can be concluded that, on the surface of zirconia, there are several kinds of oxygen atoms with different basicity participating in the coordination sphere of the surface  $O_3V=O$  species and influencing the strength of the terminal V–O bonds. It is reasonable to assume that there is a contribution to the complex band with a maximum at 1026  $cm^{-1}$  from terminal V=O groups exposed on the surface of the  $(VO_4)_n$  clusters. These surface groups can give rise to V–O stretching vibrations with a higher frequency (above 925  $cm^{-1}$ ) than those of  $VO_4$  species located in the bulk of the clusters. Ramis *et al.*<sup>40</sup> reported, for  $Mg_2(VO_4)_3$ , a surface V–O stretching mode with a higher frequency than the bulk modes. Higher frequencies of the V=O species of the top layer on multilayered vanadium oxide on zirconia was proposed also by others.<sup>13,14</sup> The origin of the weak bands at 1120–1115 and 1084  $cm^{-1}$  observed for samples 2VZ1 and 24VZ1 is not clear. They could be assigned to some pyrovanadates (see below).

The FTIR spectrum of sample 24VZ2 prepared from the diperoxovanadium(v) anion has similarities with that of bulk magnesium pyrovanadate,  $Mg_2V_2O_7$ .<sup>35</sup> This compound has a very strong and complex IR band with a maximum at 818  $cm^{-1}$  and weaker bands at 975 and 917  $cm^{-1}$  due to  $VO_3$  stretching modes. In addition, it exhibits combination bands at 1210 and 1116  $cm^{-1}$ . Based on this, the band centered at 820  $cm^{-1}$  and the broad absorption in the 1200–1050  $cm^{-1}$  region observed for sample 24VZ2 is assigned to pyrovanadate-like structures,  $(V_2O_7)_n$ . The vanadium in the pyrovanadate ion has a distorted tetrahedral coordination.<sup>35</sup> The UV/VIS data of a dry 24VZ2 sample confirm the existence of four-coordinated vanadium(v) oxo species. Under wet conditions, the coordination number of vanadium increases from 4 to 5 and 6. The shift to a higher wavelength suggests the existence of larger  $VO_x$  domains possessing higher nuclearity than the vanadium-oxo species on the 24VZ1 sample. The sample 24VZ3 [monoperoxovanadium(v) cation as a precursor] has an FTIR spectrum similar to that of 24VZ2. However, the vanadium loading of the former sample is the highest (5.1  $V^{+5} nm^{-2}$ ) which probably causes further agglomeration of the  $V_2O_7$  species. This is evident from the electronic spectrum of 24VZ3: there is an additional shift of the absorption band to higher wavelength. The band detected at 950  $cm^{-1}$  in the FTIR spectrum (Fig. 3) can be interpreted as an indication of the formation of  $V_2O_7$  species with shorter V–O bonds.

The absence of a band at 1375  $cm^{-1}$  for samples 24VZ2 and 24VZ3 rules out the presence of orthovanadate clusters. No isolated  $VO_4$  species are formed on these materials and the weak, unresolved absorption in the 1050–1000  $cm^{-1}$  region can be associated with shorter terminal V–O bonds exposed on the surface of  $(V_2O_7)_n$  domains.

In recent studies, Ghiotti *et al.*<sup>10,11,16</sup> reported FTIR data on  $VO_x/ZrO_2$  materials prepared by adsorption from ammonium metavanadate solutions at different pHs and vanadium coverages ranging from 0.045 to 11.9 V atoms  $nm^{-2}$ . Our xVZ1 materials have FTIR spectral features similar to those of the samples obtained by these authors<sup>10,11,16</sup> using the  $VO_2^+$  cation as a precursor. However, since in the cited papers there is no information about bands in the combination region, it is difficult to conclude whether the surface

$VO_x$  species characterized are identical with those discussed here. The results of the present work show that the main species formed from the  $VO_2^+$  precursor ion are  $VO_4$  groups with a  $\nu(V=O)$  surface mode at 1025–1026  $cm^{-1}$  (Fig. 3) which could correspond to the type I species (mononuclear vanadate) reported by Ghiotti *et al.*<sup>10,11,16</sup> In addition, according to these authors, there are contributions to the complex absorption in the 1100–990  $cm^{-1}$  region from polyvanadates differing in their nuclearity and denoted by type II and III, respectively. This is in contrast to the conclusion made in the present paper, that the complex character of the absorption in the 1065–980  $cm^{-1}$  region on samples 2VZ1 and 24VZ1 is due mainly to: (i) V=O stretching modes of  $VO_4$  groups directly bound to the support and containing  $O^{2-}$  ions of the zirconia with different basicity and (ii) V=O surface modes of  $VO_4$  groups exposed on the surface of  $(VO_4)_n$  clusters. Another marked difference is that in our case the increase in the vanadium loading causes an increase in the magnitude of the BET surface area of the samples relative to that of the pure support. The same phenomenon was reported also by Sohn *et al.*<sup>9</sup> Despite the similar procedure of synthesis, it seems that the  $VO_x$  species formed on the 2VZ1 and 24VZ1 samples differ in nature from those reported by Ghiotti *et al.*<sup>10,11,16</sup> The reason for this could be the higher degree of hydroxylation of zirconia used as a support in the present work.

The BET surface area of sample 24VZ2 is the highest. This can be associated with high dispersion of the  $(V_2O_7)_n$  clusters or with formation of a specific surface compound. It is possible that amorphous  $ZrV_2O_7$  is formed on the surface of the solid material. The presence of crystalline zirconium pyrovanadate on  $VO_x/ZrO_2$  was detected after high temperature calcination.<sup>9,10,15</sup>

The formation of a  $V_2O_5$  phase on the surface of the samples investigated can be excluded. This is supported by the fact that the strong combination modes typical for  $V_2O_5$  and observed at 1276 and 1200  $cm^{-1}$  (ref. 35) are not detected. In addition, in the first overtone region  $V_2O_5$  gives rise to two bands at 2020 and 1975  $cm^{-1}$ .<sup>35</sup> The former band falls in the overtone region of the  $VO_x$  species and cannot be used for identification. However, the absence of the second band in the FTIR spectra of the samples studied confirms that  $V_2O_5$  is not present as a separate phase.

## 2. Localization of the $VO_x$ species on the surface of zirconia

The adsorption of CO reveals that the surface vanadium(v) oxo species are located in the vicinity of coordinatively unsaturated (cus)  $Zr^{4+}$  ions and occupy sites of the hydroxy groups of the support. The extent of blocking of the (cus)  $Zr^{4+}$  ions and the participation of the  $Zr^{4+}$ –OH groups depend on the type of precursor ion used. For 24V1, the  $VO_x$  species are mainly located in the vicinity of the weaker Lewis acid sites of the support and on sites originally corresponding to the three-coordinated OH groups. Under the conditions of preparation of sample 24VZ1 (pH 0.5 and 0.06 mol  $dm^{-3}$   $NH_4VO_3$ ) vanadium is present in the solution in the form of the hydrated mononuclear cation,  $cis-[VO_2(H_2O)_4]^+$ .<sup>21</sup> Most probably the adsorption of these ions on zirconia takes place on (cus) oxygen ions situated in the vicinity of the zirconia  $(CO)_L$  sites. These sites are more abundant and belong to low-index faces exposed on the zirconia surface.<sup>32</sup> The three-coordinated hydroxy groups of the support (absorption band at 3395  $cm^{-1}$ ) participate probably through exchange of protons for  $VO_2^+$  species. The structures proposed above are formed after dehydration during the calcination.

When peroxovanadium(v) ions are used as precursors, the  $VO_x$  species are located in the vicinity of both types of (cus)  $Zr^{4+}$  ions,  $[(CO)_L$  and  $(CO)_H]$ . The latter sites are exposed on high-index planes and/or at defective sites (edges, kinks,

corners) of the zirconia particles.<sup>32</sup> The involvement of the more energetic (CO)<sub>H</sub> sites and all types of Zr<sup>4+</sup>-OH groups in the deposition process probably is associated with formation of peroxo bridges between zirconium(IV) and vanadium(V). The (cus) Zr<sup>4+</sup> ions are not completely blocked by the V<sub>2</sub>O<sub>7</sub> species probably due to steric factors hindering the access to these sites by the larger vanadium(V) peroxo ions. This effect is more pronounced for the diperoxo anion as a precursor (sample 24VZ2)—the number of free (CO)<sub>L</sub> sites is larger than that on the material obtained from monoperoxo ions (24VZ3). However, the general result of application of peroxovanadium(V) as precursor ions is a strong decrease in the number of (cus) Zr<sup>4+</sup> ions exposed on the surface of the support.

The solid material obtained by adsorption of diperoxovanadium(V) anions from aqueous solutions on zirconia contains dispersed pyrovanadate species, a small number of exposed Zr<sup>4+</sup> ions and possesses a high BET surface area. It could be promising in environmental catalysis, especially for diesel soot combustion.<sup>41</sup>

## Conclusions

The nature and localization of vanadium(V) oxo species deposited on the surface of zirconia by adsorption from acidic aqueous solutions of ammonium metavanadate has been studied. Two different kinds of surface VO<sub>x</sub> species are observed depending on whether dioxo- or peroxovanadium(V) ions are used as precursors. The samples prepared after adsorption of VO<sub>2</sub><sup>+</sup> and subsequent calcination contain isolated VO<sub>4</sub> groups and orthovanadate clusters, (VO<sub>4</sub>)<sub>n</sub>. The weak Lewis acid sites of the support are blocked whereas the strong ones remain free.

When vanadium(V) peroxo ions are used as precursors the vanadium loading increases approximately 2-fold. In this case, the VO<sub>x</sub> species are located in the vicinity of both types of Lewis acid site of the support. This results in a strong decrease in the number of exposed coordinatively unsaturated Zr<sup>4+</sup> ions. The predominant surface structure is identified as pyrovanadate, (V<sub>2</sub>O<sub>7</sub>)<sub>n</sub>.

The extent of participation of the Zr<sup>4+</sup>-OH depends also on the type of precursor ion used and is much larger for peroxovanadium(V) ions. On all of the samples studied, no separate V<sub>2</sub>O<sub>5</sub> phase is detected. The solid material obtained from the precursor ion [VO(O-O)<sub>2</sub>]<sup>-</sup> is characterized by a high surface area and could be promising in environmental catalysis.

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