

# Spectroscopic characterization of $\text{VO}_x/\text{ZrO}_2$ catalysts prepared using vanadium(V) oxo complexes

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## Abstract

A method for deposition of vanadium(V) oxo species on zirconia using different vanadium(V) precursor ions is described. The samples are synthesized by suspension of the support (powder) in solutions containing: (i) the dioxovanadium(V) ion,  $\text{VO}_2^+$ ; (ii) the yellow diperoxo anion,  $[\text{VO}(\text{O}-\text{O})_2]^-$  and (iii) the red monoperoxo cation,  $[\text{VO}(\text{O}-\text{O})]^+$ . The application of vanadium(V) peroxy complexes significantly increases the uptake of vanadium by zirconia. The state and localization of the  $\text{VO}_x$  species on the surface of zirconia have been studied by FTIR, UV–Vis and XP spectroscopies. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In order to have good catalytic performance, the catalysts should possess active sites that are homogeneously distributed on the surface of the support. Such catalysts are difficult to obtain by conventional routes (wet impregnation) and the development of new methods of synthesis is required.

In this paper, the possibility of application of peroxovanadium(V) ions as precursors of  $\text{VO}_x/\text{ZrO}_2$  catalysts is described. These materials are effective in the selective catalytic reduction of  $\text{NO}_x$  [1,2].

## 2. Experimental

The zirconia support was prepared by the 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 ( $0.06 \text{ mol dm}^{-3}$ ) of vanadium(V) containing three different vanadium(V) oxo species: the dioxovanadium(V) ion,  $\text{VO}_2^+$  (solution 1; prepared by dissolving ammonium metavanadate in dilute nitric acid (1:4), pH 0.5), the yellow diperoxo anion,  $[\text{VO}(\text{O}-\text{O})_2]^-$  (solution 2; obtained by dissolving ammonium metavanadate in 5%  $\text{H}_2\text{O}_2$ , pH 4.5) and the red monoperoxo cation,  $[\text{VO}(\text{O}-\text{O})]^+$  (solution 3; prepared by acidification of solution 2 with dilute nitric acid to pH 0.5).

The zirconia support (5 g, dehydrated at 623 K) was suspended in the corresponding solution ( $100 \text{ cm}^3$ ) for a given time, under constant stirring at room temperature. Then, the precipitate was washed with deionized water, dried in air at 383 K and calcined for 2 h at 723 K. The materials obtained in this way are denoted by  $x\text{VZ}_y$  where  $x$  stands for

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the time of adsorption (2 or 24 h), and  $y$  indicates the solution containing the corresponding precursor vanadium(V) oxo ion.

The UV–visible absorption spectra were measured with a Cary 5E UV–Vis–NIR spectrometer. The reference substance was either hydrated or dehydrated zirconia. The XPS spectra were taken with a KRATOS ES300 spectrometer. The binding energy of  $O_{1s}$  was used as a reference. The FTIR spectra were recorded on a Bomem MB102 FTIR (Hartman and Braun) spectrometer at a resolution of  $4\text{ cm}^{-1}$  (512 scans). Self-supporting discs of the samples were activated by heating for 1 h in a vacuum 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 of the samples

(dehydrated at 623 K) 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  $V^{5+}$  ions in 0.03%  $H_2O_2$ .

### 3. Results and discussion

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

The FTIR spectra in the OH stretching region of the solid materials studied are shown in Fig. 1(A). The bands observed in the spectrum of pure zirconia

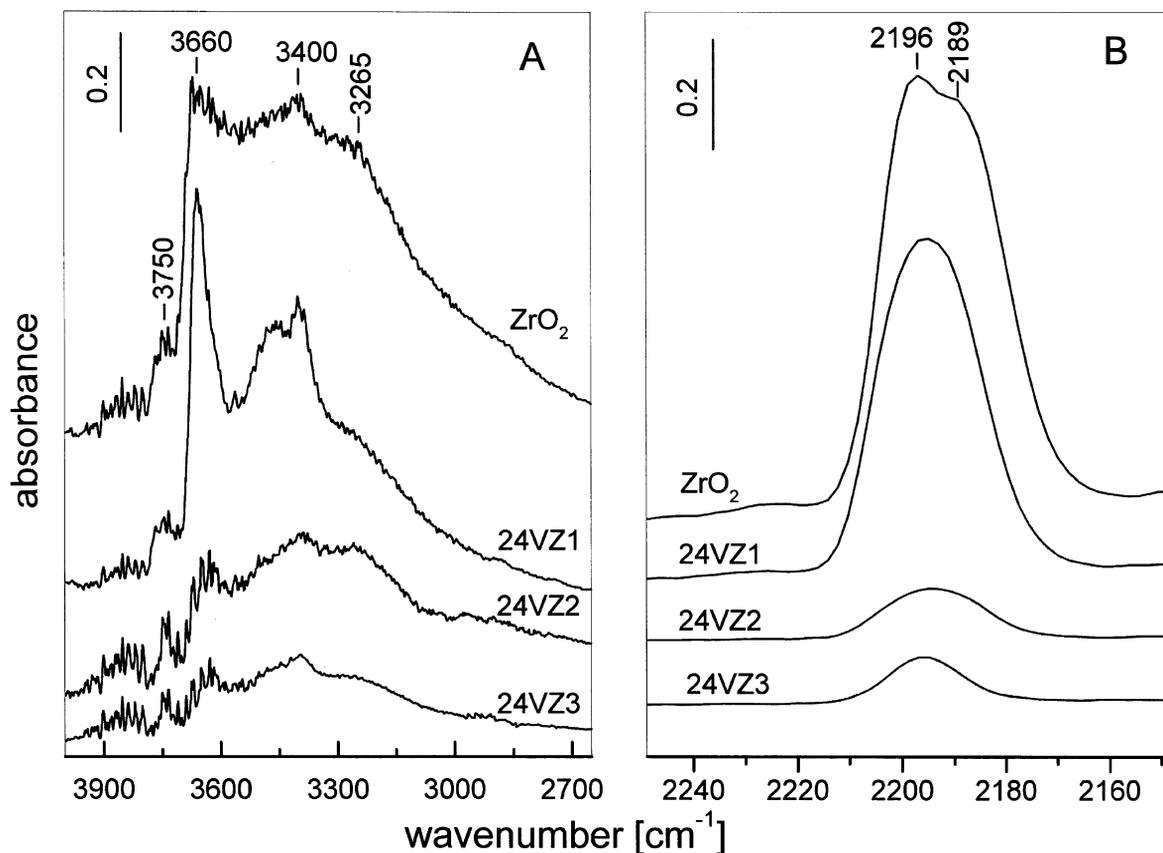


Fig. 1. (A) FTIR spectra of the activated samples in the hydroxyl region. (B) FTIR spectra of adsorbed CO (4 kPa) at 298 K on the activated samples.

are assigned to terminal hydroxyls ( $3750\text{ cm}^{-1}$ ) and bridged OH groups coordinated to two ( $3660\text{ cm}^{-1}$ ) and three Zr atoms ( $3400\text{ cm}^{-1}$ ) [3]. The absorption at  $3265\text{ cm}^{-1}$  is attributed to H-bonded OH groups. The sample 24VZ1 prepared from dioxovanadium(V) cation, displays spectrum similar to that of zirconia with somewhat more narrow bands. The intensities of the three-coordinated OH groups of the support are reduced relative to the two-coordinated hydroxyls. In the case of samples 24VZ2 and 24VZ3, the total population of the surface OH groups of zirconia decreases strongly. It is difficult to conclude if surface OH groups of type  $\text{V}^{5+}\text{-OH}$  are formed. The latter are characterized by absorption at  $3660\text{ cm}^{-1}$  [4–6]. The absorption in this region decreases with an increase in the vanadium loading.

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. 1(B)). 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 [7].

Based on the fact that CO does not form carbonyls with  $\text{V}^{5+}$  ions [4–6], the following conclusions are made from the FTIR: (i) in the case of 24V1 ( $\text{VO}_2^+$  precursor ions), the  $\text{VO}_x$  species complete the coordination sphere of the weaker Lewis sites of the support and occupy a certain amount of the sites originally corresponding to the three-coordinated OH groups; (ii) the amount of exposed  $\text{Zr}^{4+}$  ions decreases remarkably when peroxovanadium(V) ions are used as precursors. The  $\text{VO}_x$  species on the

surfaces of samples 24VZ2 and 24VZ3 are coordinated with both types of Lewis acid sites of the support and occupy a significant part of the sites originally corresponding to all types of  $\text{Zr}^{4+}\text{-OH}$  groups. The involvement of the more energetic  $(\text{CO})_{\text{H}}$  sites and all kinds of zirconia hydroxyls could be associated with the formation of peroxo bridges between zirconium (IV) and vanadium(V) during adsorption from the peroxo solutions.

### 3.2. Oxidation state of vanadium and surface concentration

According to the XPS data, the oxidation number of vanadium in the  $x\text{VZ}_y$  samples is +5 ( $\text{V}_{2\text{p } 3/2}$  peak at  $517\text{ eV}$ ) [5,6,8]. The data of the chemical analysis and XPS are given in Table 1. The number of theoretical monolayers in the last column is estimated by taking into account the localization of the  $\text{VO}_x$  species and the existence of four-coordinated  $\text{V}^{5+}$  ions in the activated samples (see below).

### 3.3. Coordination number of vanadium(V) in the surface $\text{VO}_x$ species

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 sample 24VZ2, recorded immediately after the activation in the IR cell, is also presented. The increase in the vanadium coverage causes a noticeable red shift in the absorption maxima. This accounts for the occurrence of progressive oligomerization through

Table 1  
Physico-chemical characteristics of the samples investigated

Sample	Precursor ion	$\text{V}^{5+}$ loading, wt. %	S, $\text{m}^2/\text{g}$	Surface ratio V:Zr (XPS)	Surface concentration, $\text{V}^{5+}/\text{nm}^2$ (chemical analysis)	Theoretical monolayers of $\text{V}_2\text{O}_5$ on zirconia <sup>a</sup>	Theoretical monolayers of $\text{O}_3\text{V=O}$ units on zirconia <sup>b</sup>
$\text{ZrO}_2$	–	–	69	–	–	–	–
2VZ1	$\text{VO}_2^+$ , pH 0.5	0.6	75	–	1.0	0.1	0.4
24VZ1	$\text{VO}_2^+$ , pH 0.5	1.3	90	(1.1:100)	2.2	0.2	1.0
24VZ2	$[\text{VO}(\text{O}-\text{O})_2]^-$ , pH 4.5	2.2	167	5.8:100	3.8	0.4	1.6
24VZ3	$[\text{VO}(\text{O}-\text{O})]^+$ , pH 0.5	3.0	91	9.6:100	5.1	0.5	2.2

<sup>a</sup> Calculated from the  $\text{V}^{5+}$  loading, the surface area of the support and the estimated area occupied by  $\text{VO}_{2.5}$  unit [9] ( $1.05 \times 10^{-19}\text{ m}^2$ ).

<sup>b</sup> Calculated assuming one V atom per three Zr atoms and surface concentration of seven  $\text{Zr}^{4+}$  ions/ $\text{nm}^2$  for complete dehydroxylated zirconia [7].

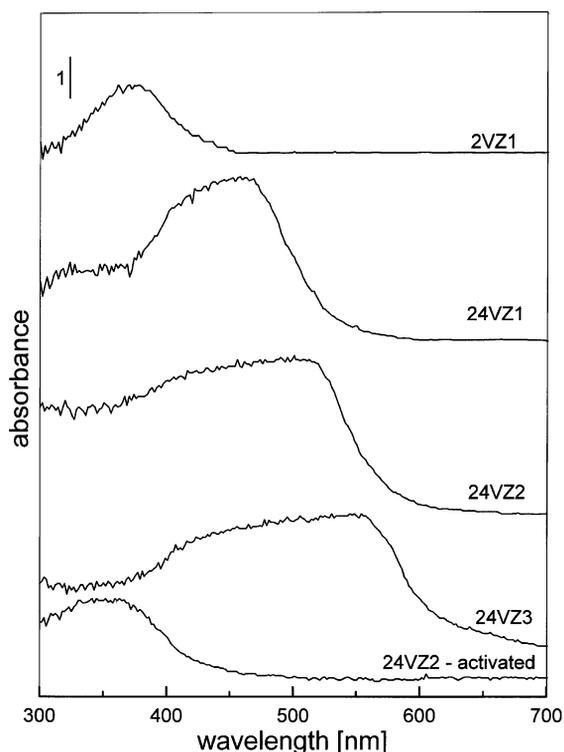


Fig. 2. The absorption spectra in the visible range of the samples studied exposed to ambient conditions, and of sample 24VZ2 immediately after the activation.

the formation of V–O–V linkages leading to agglomeration of the immobilized  $\text{VO}_x$  species [10,11]. The differences in the spectra between the dehydrated (activated) and hydrated (exposed to ambient conditions) 24VZ2 samples can be explained by the tendency of coordinatively unsaturated  $\text{VO}_x$  species to complete their coordination sphere adding water as ligands [10,11]. The absorption bands are typical for  $\text{V}^{5+}$  ions in an octahedral environment (charge transfer band  $\text{O} \rightarrow \text{V}^{5+}$  at 450–550 nm), five- (400–415 nm) and four-coordinated vanadium(V) (325–375 nm) [6,10,11].

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

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) (Fig. 3). This suggests that two different kinds of  $\text{VO}_x$  species are deposited on zirconia, depending on whether dioxo or peroxovanadium(V) ions are used as precursors. For samples 2VZ1 and 24VZ1, the band at 1375  $\text{cm}^{-1}$  with a shoulder at 1335  $\text{cm}^{-1}$  and the complex absorption in the region, 925–800  $\text{cm}^{-1}$ , grow with an increase in the vanadium content. Similar bands were reported in the spectrum of bulk  $\text{Mg}_3(\text{VO}_4)_2$ : 861  $\text{cm}^{-1}$  with satellites at 915 and 833  $\text{cm}^{-1}$  due to  $\nu_{\text{as}}(\text{VO}_4)$  modes and strong band at 1347  $\text{cm}^{-1}$  assigned to a combination of the symmetric stretching of the  $\text{VO}_4^{3-}$  ion with a deformation mode [12]. Based on this, it can be concluded that orthovanadate-like phases, i.e.  $(\text{VO}_4)_n$  clusters, are formed on the surface of the samples of the  $x\text{VZ1}$  series, characterized by the complex band with a maximum at 870–860  $\text{cm}^{-1}$  ( $\text{VO}_4$  stretching mode, observed in the case of 2VZ1 sample) and the combination bands at 1375 and 1335  $\text{cm}^{-1}$ . The sharp asymmetric band in the 1065–980  $\text{cm}^{-1}$  region (with a maximum at 1026–1024  $\text{cm}^{-1}$ ) can be attributed to surface V=O groups [5,6,10,13]. The complex character of this absorption can be explained assuming a superimposition of bands due to V=O stretching modes of isolated  $(\text{ZrO})_3\text{V}=\text{O}$  species and terminal V=O groups exposed on the surface of  $(\text{VO}_4)_n$  clusters.

The FTIR spectrum of sample 24VZ2, prepared from diperoxovanadium(V) anion, has similarities with that of bulk magnesium pyrovanadate,  $\text{Mg}_2\text{V}_2\text{O}_7$  [12]. This compound has a strong IR band with maximum at 818  $\text{cm}^{-1}$  due to  $\text{VO}_3$  stretching modes and combination bands at 1210 and 1116  $\text{cm}^{-1}$  [12]. Based on this, the band centered at 820  $\text{cm}^{-1}$  and the broad absorption in the 1200–1050  $\text{cm}^{-1}$  region (Fig. 3) are assigned to pyrovanadate-like structures,  $(\text{V}_2\text{O}_7)_n$ . The weak, unresolved absorption in the 1050–1000  $\text{cm}^{-1}$  region can be associated with shorter terminal V–O bonds exposed on the surface of  $(\text{V}_2\text{O}_7)_n$  domains. The sample 24VZ3 (monoperoxovanadium(V) cation as a precursor) has an FTIR spectrum similar to that of the 24VZ2. However, the vanadium loading of the former sample is the highest (5.1  $\text{V}^{5+}/\text{nm}^2$ ), which could cause further agglomeration of the  $\text{V}_2\text{O}_7$  species. The band detected at 950  $\text{cm}^{-1}$  in the FTIR spectrum is attributed to  $\text{V}_2\text{O}_7$  species with shorter V–O bonds (Fig. 3).

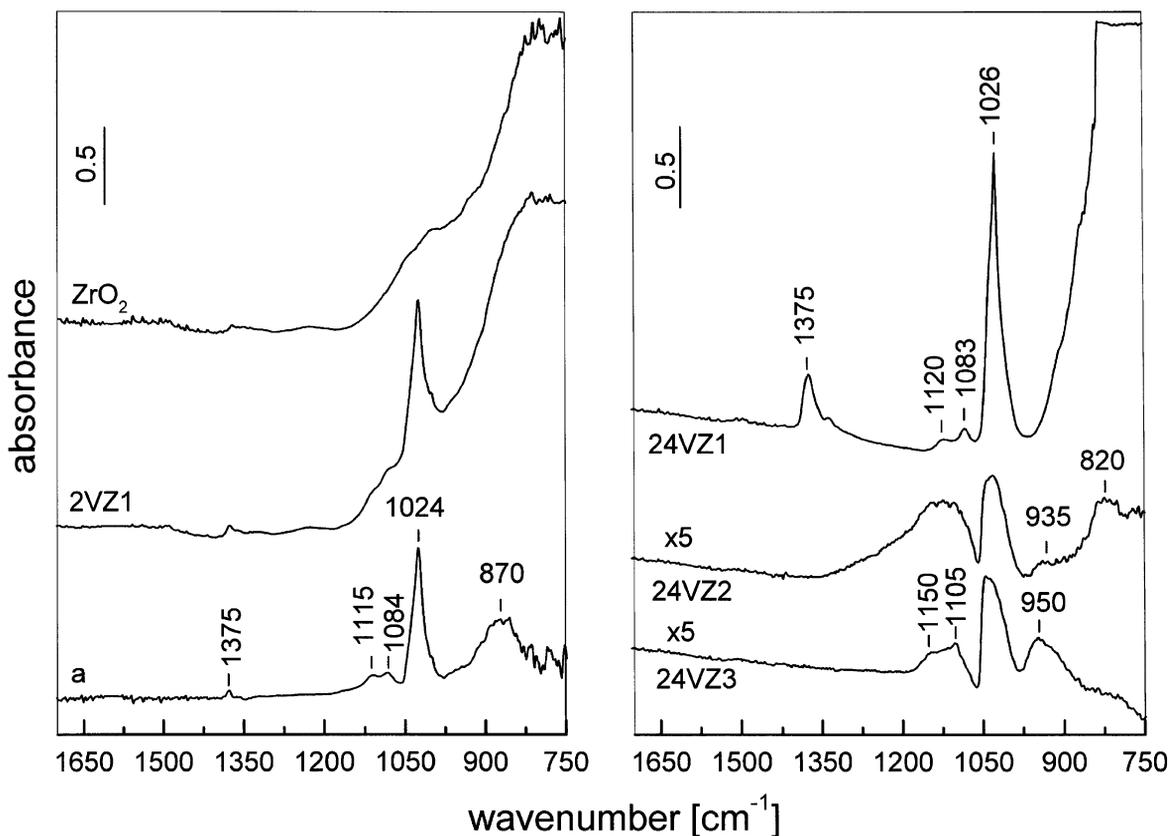


Fig. 3. The FTIR spectra of the activated samples. The spectra (a), 24VZ2 and 24VZ3 are obtained by subtraction of the spectrum of  $\text{ZrO}_2$  from the full spectra of samples 2VZ1, 24VZ2 and 24VZ3, respectively.

The increase in vanadium loading causes an increase in the magnitude of the BET surface area of the samples relative to that of the pure support (Table 1). The BET surface area of sample 24VZ2 is the highest. This can be associated with high dispersion of the  $(\text{V}_2\text{O}_7)_n$  clusters or with the formation of a specific surface compound. It is possible that amorphous  $\text{ZrV}_2\text{O}_7$  is formed on the surface of the solid material.

#### 4. Conclusions

The application of vanadium(V) peroxo complexes for ion exchange significantly increases the uptake of vanadium by zirconia. The solid material obtained by adsorption of diperoxovanadium(V) an-

ions contains dispersed pyrovanadate species, small amounts of exposed  $\text{Zr}^{4+}$  ions, and possesses high BET surface area. It could be promising in oxidation and environmental catalysis.

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