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Sub-monolayer V_2O_5–anatase TiO_2 and Eurocat catalysts: IR, Raman and XPS characterisation of VO_x dispersion

F. Chiker, J.Ph. Nogier*, J.L. Bonardet

Systèmes Interfaciaux à l'Echelle Nanométrique (SIEN), CNRS FRE 2312, B.P. 196, Université P. et M. Curie,
4 Place Jussieu, F-75252, Paris Cedex 05, France

Abstract

VO_x–TiO_2 catalysts with vanadium loading less than that of a monolayer have been prepared either by impregnation in aqueous media from solutions of V(V) or V(IV) at different concentrations and pH, or by grafting in anhydrous media on anatase supports with surface areas of 10, 150 and 350 $m^2\,g^{-1}$. Their characterisation by XPS, DRIFT and Raman spectroscopy, compared to that of EUROCAT EL10V1 and V8 reference catalysts, shows that the dispersion of the load depends on the mode of preparation and is not necessarily equal to 1.

Keywords: V_2O_5; Anatase TiO_2; Spectroscopy; IR; Raman; XPS; Dispersion

1. Introduction

Catalysts consisting of vanadium oxide deposited on anatase TiO_2 continue to inspire research because of their interest in selective oxidation reactions [1,2], for the elimination of nitrogen oxides [3,4] or ammoxidation [5–7]. Much work has been done on the characterisation of the VO_x deposit by IR [2–4,7–9], Raman [2–4,10,11], EPR [2,3,7] and NMR spectroscopy [2,3,12,13]. Wachs et al. [14,15] recently presented reviews of this work. Attention is paid increasingly to the determination of dispersion of the deposit, for which purpose adsorption has been used as well as the kinetics of the reaction of NH_3, of NO [4,16,17], of methanol [18], reduction–reoxidation [2,3,16,19,20,21] and Raman spectroscopy [4]. It is accepted that for loadings less than the monolayer the deposit consists of mono- and polyvanadates; beyond this limit the crystalline oxide V_2O_5 appears. However, the XPS characterisation of catalysts with low vanadium loadings led us to reconsider this statement and to compare the results obtained by this technique with those of IR and Raman spectroscopy. Moreover, this characterisation allows us to compare the modes of vanadium deposition: adsorption of vanadium ions V(IV) or V(V) in aqueous media at different pH, and grafting in anhydrous media.

2. Experimental conditions

2.1. Catalyst preparation

Four different supports were used: practically identical non-porous anatases of 10 $m^2\,g^{-1}$ (Tioxide: Tiox et Millenium Industrie, EL10), an anatase of 350 $m^2\,g^{-1}$ (PC 500, Millenium Industrie) and a mesoporous anatase of 150 $m^2\,g^{-1}$. This latter was prepared in the laboratory from titanium tetraethoxide

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* Corresponding author. Fax: +33-1-4427-5536.
E-mail address: nogier@ccr.jussieu.fr (J.Ph. Nogier).

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(TEOT) by the method described by Yue and Gao [22]: the source of titanium, TEOT (11.4 g), and 5.8 g of triblock copolymer, $(EO)_{20}(PO)_{70}(EO)_{20}$ are dissolved in 40 g of ethanol. After 1 h of stirring at ambient temperature a mixture of water (24 g) and ethanol (46 g) is added dropwise to the solution. The mixture is then stirred for 48 h, after which water is added to bring the H_2O/TiO_2 molar ratio up to 90. Hydrothermal treatment is carried out in a Teflon autoclave at 80 °C for 24 h. The filtered product is dried at 100 °C and then calcined in air at 350 °C for 4 h. This temperature was chosen in order to avoid any superficial migration of vanadium species over the surface [14].

2.2. Vanadium deposition

The different anatases were impregnated at equilibrium with solutions of vanadium V(V) (NH_4VO_3 plus HNO_3) in excess at pH = 1, 4 and 5.5 at concentrations between 5×10^{-3} and 4×10^{-2} mol l^{-1}. Which ion predominates in the solution depends on the pH: VO_2^+ at pH = 1 then negatively charged decavanadates at pH = 4 or 5.5 [23,24]. Some samples were prepared by impregnation with a flowing solution at pH = 5.5, the vanadium V(V) concentration being 5×10^{-5} mol l^{-1}. In this solution the major species is $VO_2(OH)_2^-$. At such pH the surface of the anatase, whose isoelectric point is 5.5, is positively charged. Impregnation by vanadyl oxalate was performed from solutions of concentration 5×10^{-2} to 0.4 mol l^{-1} at pH = 1.2. The EUROCAT EL10V1 and V8 catalysts were prepared by Garcin et al. [2].

Grafting on TiO_2 was performed by means of vanadyl *tert*-butylate in toluene distilled over sodium and benzophenone. TiO_2 was first dehydrated in O_2 at 300 °C and grafting carried out in the same apparatus with the exclusion of air. After vanadium deposition these samples were calcined in oxygen at 350 °C.

The samples are designated on the basis of the name of the anatase: Tioxide (Tiox), EL10, PC500, or mesoporous TiO_2 (MP) followed by the mode of deposition: (i) impregnation by vanadyl oxalate (ox), (ii) impregnation by V(V) characterised by the pH, (iii) grafting (gr) and followed finally by the concentration. For example, Tiox-ox-0.1 denotes tioxide anatase impregnated by vanadyl oxalate at a concentration of 0.1 mol l^{-1}.

3. Characterisation

3.1. Chemical analysis

Samples were analysed by ICP after complete solution in sulphuric acid or dissolution of surface vanadium in sulphuric acid followed by redox analysis of vanadium by iron [2].

3.2. Specific surface areas and porosity

Specific surface areas and porosities were determined on an automatic Micromeretics ASAP2010 apparatus.

3.3. XPS study

The XPS spectra were obtained on an SSI M-Probe apparatus with an Al cathode (1456.86 eV) and a monochromator. To avoid photoreduction of V(V) the power of the X-ray beam was limited to 200 W [2]. The spectra were treated using a Shirley baseline. The peak profile was taken as 75% Gaussian which minimises the deviation of the calculated curve from the experimental points. The ratio of the sensitivity factors for V and Ti was determined from pure TiO_2 and V_2O_5 [25]. The experimental value is 1.36 ± 2% [26]. The value used by the program associated with the ESCA apparatus is 1.160. The electron mean free path was considered to be practically identical at 1.5 nm in TiO_2 and V_2O_5 [2,27].

3.4. DRIFT study

The IR spectra were obtained on a Bruker Vector 22 spectrometer, the sample being kept in oxygen flow at the chosen temperature, usually 200 °C, in a Harrick cell with KBr windows, 600–2000 scans were performed. The acquisition temperature of the spectra must allow the observation of the OH bands by desorbing physically adsorbed water, while avoiding the destruction of the TiOH and VOH groups. IR study of the EUROCAT EL10V8 catalyst in oxygen between 100 and 500 °C showed that above 300 °C a large proportion of the OH groups are destroyed. Our study was therefore performed at 200 °C. The spectra are presented smoothed after subtraction of a polynomial baseline.

3.5. Raman study

The first series of Raman spectra was recorded in air. The excitation wavelength is 514.5 nm, the power 25 mW and the number of scans is 25. The other spectra were measured at the same wavelength on a DILOR XY multichannel spectrometer with a power of 50 mW, an acquisition time of 100 s for the general spectrum and 500 s for the vanadium region (850–1700 cm^{-1}). Samples were observed in air without pretreatment or in sealed tubes after heating for 1 h at 200 °C then at 300 °C under 13 kPa (100 Torr) of oxygen for 30 min. We checked that this treatment assured that the vanadium was in the (V) oxidation state.

4. Results and discussion

4.1. Chemical analysis

The amounts of vanadium deposited, the specific surface areas and the superficial vanadium densities are presented in Table 1. The values of the superficial densities correspond to a virtual dispersion of unity for the distribution of the vanadium species in a monolayer. The vanadium loading is expressed as a fraction, X, of a monolayer taking the value of the effective area of the vanadium atom as $\sigma_V = 0.1256\,nm^2$ [28] considered to be equivalent to that of V in V_2O_5. In the polyvanadates the area of V is 0.1134 nm^2 [2].

4.2. XPS study

First of all, it must be noted that EL10 support is non-porous, consequently vanadium species are deposited on the outer surface of the sample. The intensity ratios of the $V_{2p_{3/2}}$ and $Ti_{2p_{3/2}}$ peaks $(V/Ti)_{XPS}$ are plotted against the atomic ratio (V/Ti) atom (Fig. 1). The response of the catalysts prepared by vanadyl oxalate impregnation follows a curve whose slope decreases as the load increases, which shows that the dispersion decreases. This decrease becomes very clear once the vanadium loading reaches the value of the half monolayer. It should be noted that EL10V1 is no different from the other catalysts in this series, even though it is prepared somewhat differently by progressive concentration of the oxalate. For this catalyst the coverage by VO_x, calculated by the "towers on a bare surface" model [2], is 0.1 for a mean deposit thickness of 3 nm. The $(V/Ti)_{XPS}$ ratio expected for unit coverage, that is, a dispersion of 100%, would be 0.245. The catalysts prepared by impregnation by V(V) ions at pH = 1 and 4 show a higher vanadium response than those of the previous series. Finally, the catalyst loaded at pH = 5.5 by a $5 \times 10^{-5}\,mol\,l^{-1}$ solution where the $VO_2(OH)_2^-$ species predominates, gives the highest vanadium response and can be considered as corresponding to the greatest dispersion, but the loadings reached remain low for very high impregnation times (2–7 days). The results of grafting in an anhydrous medium are not presented in this figure. Despite all the precautions taken they are

Table 1
The amounts of vanadium deposited, the specific surface areas and the superficial vanadium densities are given below

Sample	Specific surface area ($m^2\,g^{-1}$)	Vanadium content, n(V) ($mol\,g^{-1} \times 10^{+5}$)	Atomic density, d(V) ($atom\,m^{-2} \times 10^{+18}$)	Charge expressed as fraction of monolayer, X(V) monolayer
EL10V8	10	88.0	53	5.4
EL10V1	10	11.0	6.62	0.62
Tiox-ox-0.05	10	1.6	0.97	0.10
Tiox-ox-0.1	10	4.37	2.63	0.27
Tiox-ox-0.2	10	10.5	6.31	0.65
Tiox-ox-0.4	10	17.4	10.4	1.07
PC500-2 × 10^{-2} at pH = 1	350	52.2	0.9	0.09
PC500-gr	350	103.6	1.78	0.18
MP-10^{-2} at pH = 1	150	33	1.32	0.14
MP-2 × 10^{-2} at pH = 1	150	43.2	1.73	0.18
MP-3 × 10^{-2} at pH = 1	150	65.8	2.64	0.27
MP-4 × 10^{-2} at pH = 1	150	69.7	2.8	0.28
MP-2 × 10^{-2} at pH = 5.5	150	70.7	2.8	0.29

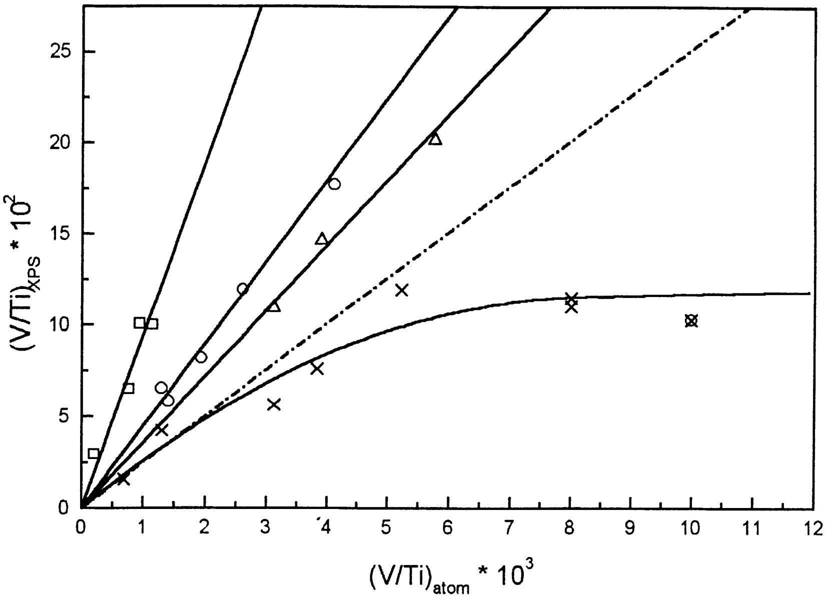

Fig. 1. Ratio $(V/Ti)_{XPS}$ of XPS $V_{2p_{3/2}}$ and $Ti_{2p_{3/2}}$ signals in terms of the atomic ratio $(V/Ti)_{atom}$: (☐) EL10 at pH = 5.5 (2–7 days, 5×10^{-5} mol l^{-1}), (○) EL10 at pH = 1, (△) EL10 at pH = 4, (- - -) slope at the origin, (×) EL10-ox, (⊗) EL10V1.

irregular, and the dispersion obtained varies between the values corresponding to the two extreme curves presented in Fig. 1. As for the vanadium XPS response, it must be noted that on the catalysts with the highest dispersions, this response exceeds the maximum value which can be calculated with the simple "towers on a bare surface" model [2,25], the limit represented in Fig. 1 by the tangent at the origin (dotted line) of the response curve for the catalysts prepared by oxalate impregnation. Considering the mechanism of vanadium attachment, there are two questions about the adsorption of the VO_2^+ ion, which is predominant in the solution at pH = 1, the anatase surface then being positively charged. Is the ion which is adsorbed really VO_2^+ or a negatively charged decavanadate in equilibrium with the latter? Are these decavanadates, consisting of three superposed planes of VO_6 octahedra [23,24], precursors of V_2O_5 crystallites? Raman and IR spectroscopy provide part of the answer to this question.

4.3. IR study

The spectrum of V_2O_5 (Fig. 2a) is characterised in the 1800–2100 cm^{-1} region by two maxima at about 1970 and 2012 cm^{-1}. These bands can be assigned to the combination of the fundamental V=O stretching bands of V_2O_5 as reported by Busca and Zecchina [29]. The presence of these two same maxima shows that there is crystalline V_2O_5 in the EL10V8 (Fig. 2b), EL10V1 (Fig. 2c) and Tiox-ox-0.4 (Fig. 2d) catalysts. It should be remembered that X-ray diffraction showed clearly that there is crystalline V_2O_5 in EL10V8, and rather less clearly in EL10V1 V_2O_5 being revealed by only one peak at this at the limit of detection. The catalysts prepared by impregnation at pH = 1 have spectra (Fig. 3) very different from the previous ones with a single maximum at 2042 cm^{-1}. The same spectral shape is found for catalysts prepared by impregnation at pH = 5.5 (MP-2 $\times 10^{-2}$) and generally for those prepared by grafting, the results of which are, however, random in terms of dispersion. This band was observed by Baiker and co-workers [30] at 2035 cm^{-1} in argon and at 2040–2045 cm^{-1} in oxygen. In agreement with Busca and co-workers [31,32] and Wachs [33], it is attributed to the first harmonic of the symmetrical V=O vibration in the mono-oxo groups.

The Tiox-ox catalysts prepared by oxalate impregnation give spectra (Fig. 2e–g) which depend on

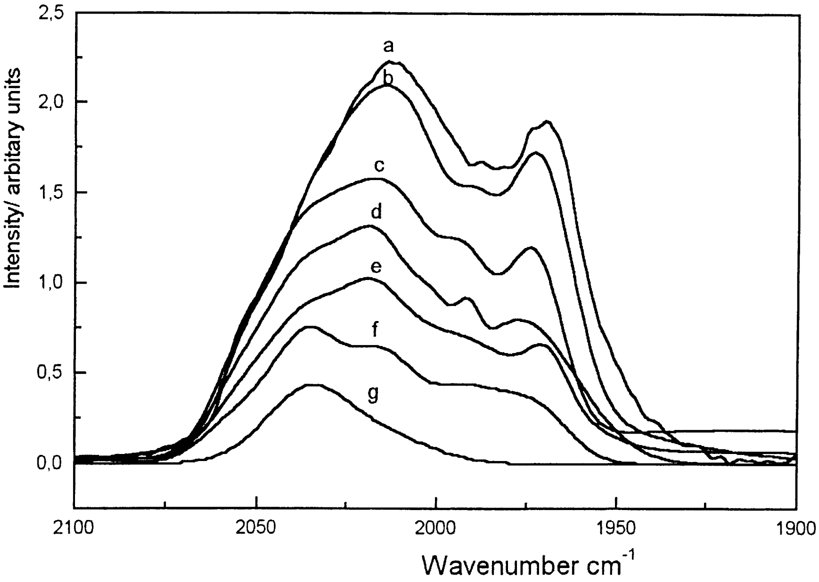

Fig. 2. IR spectra in O_2 at 200 °C of: (a) V_2O_5; (b) EL10V8; (c) EL10V1; (d) Tiox-ox-0.4, $X = 1.07$; (e) Tiox-ox-0.2, $X = 0.65$; (f) Tiox-ox-0.1, $X = 0.27$; (g) Tiox-ox-0.05, $X = 0.1$.

the loading, between the two previous forms, which indicates that the deposit consists in part of crystalline V_2O_5. Amongst these, Tiox-ox-0.1 and Tiox-ox-0.2 have loadings less than the monolayer. To evaluate the fraction of the area of the signal due to dispersed species, we subtract from the spectrum of the sample the spectrum of V_2O_5 weighted so that the intensities of the two signals coincide at 1970 cm^{-1}. This value

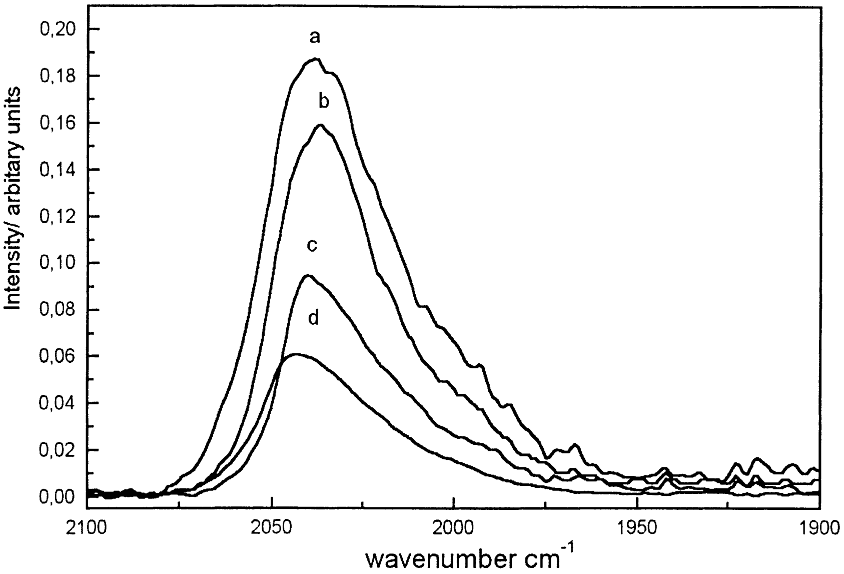

Fig. 3. IR spectra in O_2 at 200 °C of: (a) MP-4 x 10^{-2} at pH = 1, $X = 0.28$; (b) MP-3 x 10^{-2} at pH = 1, $X = 0.27$; (c) MP-2 x 10^{-2} at pH = 1, $X = 0.18$; (d) MP-10^{-2} at pH = 1, $X = 0.14$.

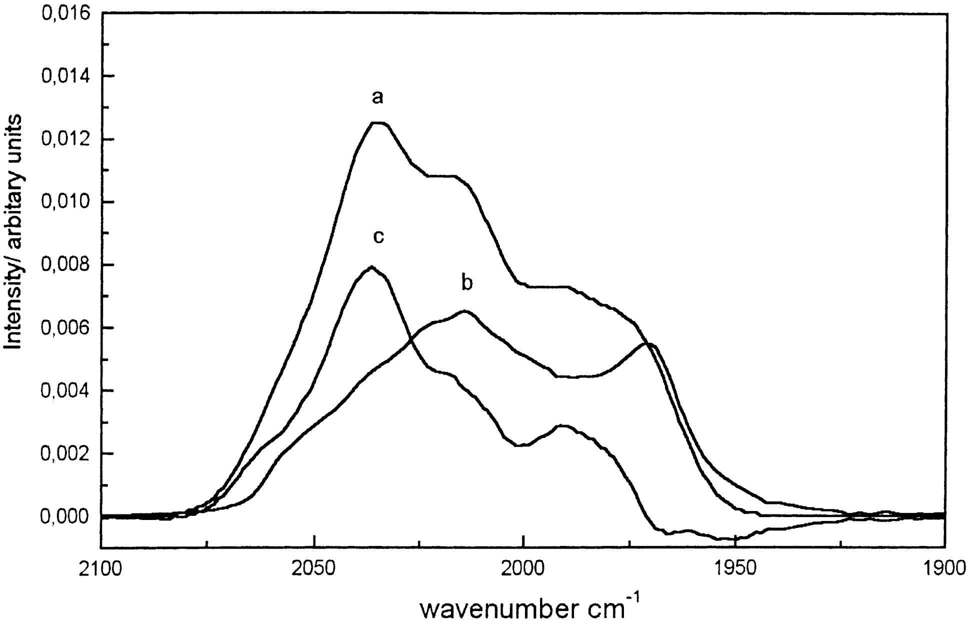

Fig. 4. IR spectra of (a) Tiox-0.1 (b) V_2O_5 multiplied by weighting factor (c) difference a−b.

is chosen because the dispersed species have zero intensity at this point (Fig. 4).

This subtraction gives a peak with a maximum at 2037 cm^{-1} (Fig. 4c) like that of the dispersed species. It allows us to evaluate the fraction of the area of the peak due to crystalline V_2O_5 and to dispersed species. The results of this operation for the Tiox-ox samples are presented in Table 2.

4.4. Raman characterisation

Fig. 5 shows the spectra recorded in air for catalysts prepared either by oxalate impregnation or by impregnation with V(V) solution at pH = 1 and 4.

Table 2
Fractions of the area of the signal attributed to crystalline V_2O_5 and to mono-oxo vanadyl groups

Sample	V content monolayer	$X(V_2O_5)$, %	$X(V{=}O)$, %
Tiox-ox-0.05	0.10	0	100
Tiox-ox-0.1	0.27	56.5	43.5
Tiox-ox-0.2	0.65	61.6	38.4
Tiox-ox-0.4	1.07	64.6	36.4
EL10V1	0.62	69.6	30.4

The broad band (spectra b–d) with a maximum at about 990 cm^{-1} has been attributed to polyvanadates. The main reason for this attribution is the shift of the maximum, observed here, with the vanadium loading [30]. One observes the sharp peak at about 995 cm^{-1} for the EL10-ox-0.1 catalyst (spectrum d) characteristic of crystalline V_2O_5 for a loading lower than the half monolayer ($X(V) = 0.27$). The same peak is observed for EL10V1. This peak corresponds, however, to two vibrations, one of which is attributed to crystalline V_2O_5 and the other to hydrated V=O in the monovanadate [31,32]. Fig. 6 shows the spectra of EL10V8 and EL10V1 obtained in O_2 at 25 °C (after treatment in O_2 at 300 °C). They show the same band at 1090 cm^{-1}. That at 995 cm^{-1} characteristic of V_2O_5 is still present but is very weak for EL10V1. A band at 1022 cm^{-1} can be seen for EL10V8 and doubtless corresponds to stretching vibrations of the V=O bond but perhaps not in the configuration of an isolated monovanadate, normally characterised by a band at 1030 cm^{-1}. Fig. 7 shows the spectra of the catalysts prepared by impregnation at pH = 1 and 5.5. Their shape is very different from that of the previous ones; they are dominated by a band at about 1030 cm^{-1} attributed to isolated monovanadates. This shows that

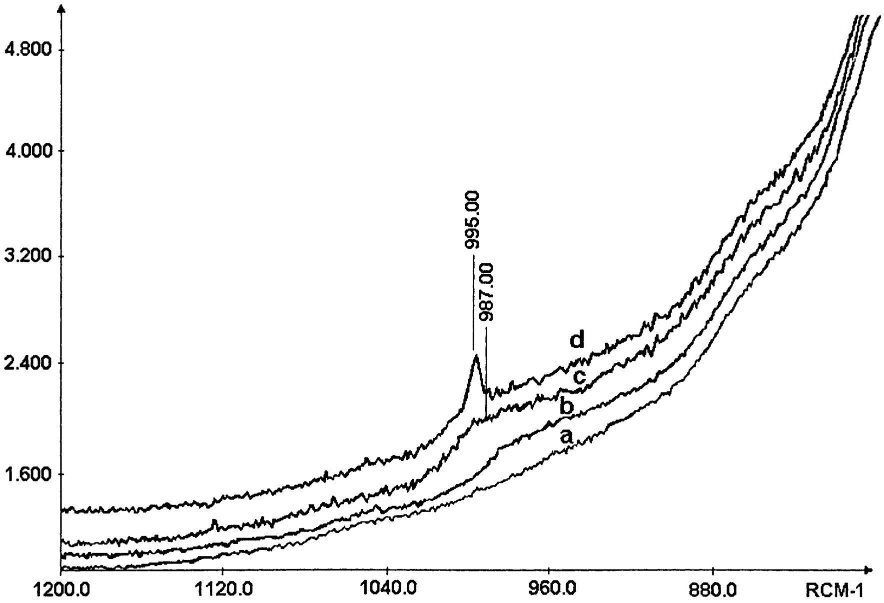

Fig. 5. Raman Spectra of catalyst: (a) EL10-ox-2.5 × 10^{-2}; (b) EL10-9 × 10^{-3} at pH = 1; (c) EL10-2 × 10^{-2} at pH = 4; (d) EL10-ox-0.1. Recorded in air, 25 mW, 25 scans.

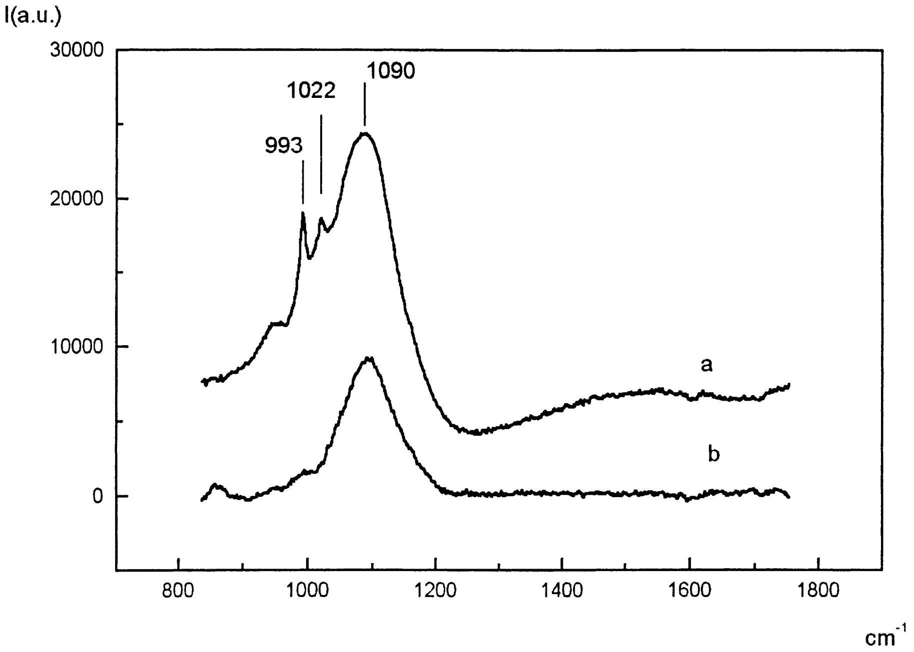

Fig. 6. Raman spectrum of (a) EL10V8 in O_2; (b) EL10V1 in O_2. Acquisition time is 500 s.

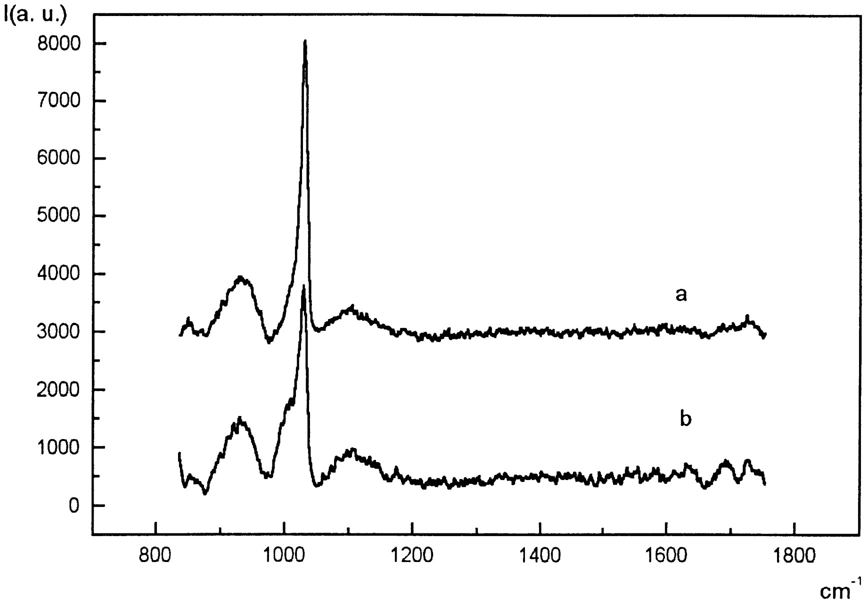

Fig. 7. Raman spectrum in O_2 of (a) MP-2 × 10^{-2} at pH = 1; (b) MP-2 × 10^{-2} at pH = 5.5. Acquisition time is 500 s.

while adsorption at pH = 5.5 is certainly that of decavanadates (as at pH = 4), which are predominant in the solution and negatively charged, the result is finally very close to that at pH = 1, the decavanadates being, upon adsorption or calcination, dispersed into isolated vanadyl species.

5. Conclusion

The XPS, IR and Raman spectroscopic characterisation of catalysts with a loading less than a monolayer leads to coherent results, showing that the dispersion of the VO_x deposit obtained depends on the mode of preparation if the calcination temperature of the sample remains below 370 °C [14,26]. The adsorption of vanadyl oxalate leads systematically to the lowest dispersion. The adsorption of vanadium V(V) at pH = 1 leads to deposits with high dispersions close to those obtained by adsorption of decavanadates at pH = 4 or 5.5 at a concentration above 10^{-3} mol l^{-1}. The maximum dispersion is obtained by grafting in anhydrous media or by adsorption of $VO_2(OH)_2{}^-$ ion at pH = 5.5 at a concentration of 5 × 10^{-5} mol l^{-1}. Simple models of the XPS response of oxide catalysts deposited on oxide support should be refined in order to account for the dispersion of the deposit at low loadings below the monolayer.

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