JOURNAL OF CATALYSIS **122**, 312–319 (1990)

EXAFS Investigation of Vanadium–Phosphorus Catalysts with Different P/V Ratios

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Received July 8, 1988; revised September 1, 1989

Vanadium–phosphorus catalysts with different P/V ratios (0.93–1.28) have been investigated by EXAFS and XANES applied to the *K*-edge region of vanadium. When looked at from the pre-edge peak, vanadium appeared in the 4+ state after drying, while after calcination at 673 K both 4+ and 5+ states occurred simultaneously on samples with P/V > 1. EXAFS revealed that by changing chemical composition, structural variations occur around vanadium. On dried samples, the coordination number decreased from 5 to 4. On calcined samples, the longest V–O distance increased from 1.91 to 1.96 Å. The possible influence on the catalytic activity is discussed.

1. INTRODUCTION

In a recent paper (*1*) we investigated the catalytic activity for *n*-butane oxidation of vanadium–phosphorus oxides having different P/V ratios. Their physicochemical characterization was made by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and extended X-ray absorption fine structure spectroscopy (EXAFS). The latter concerned the collection of P *K*-edge spectra and allowed us to conclude that an excess of phosphorus, although responsible for a dramatic increase (one order of magnitude) in the specific conversion, does not induce relevant structural effects around P atoms, i.e., variation of the coordination geometry and interatomic distances.

In the present work we examine the preedge and the EXAFS *K*-edge regions of vanadium, thus completing, as anticipated previously (*1*), the structural investigation of the catalyst samples. The application of EXAFS and XANES (X-ray absorption near-edge structure) techniques in heterogeneous catalysis has increased in recent years and has been widely reviewed (*2, 3*). Such studies offer a valuable contribution to the knowledge of the structural and electronic situation of a specific atom, mainly in the presence of structural disorder, typical of heterogeneous catalyst samples.

2. EXPERIMENTAL

Catalysts were prepared by adding a suitable amount of aqueous H_3PO_4 to a solution formed by stirring V_2O_5 and HCl in water for 4 h at room temperature (RT). Pale green solids with P/V atomic ratios in the range 0.93–1.28 were obtained after evaporation to dryness and treatment at 423 K in air for 2 h. Calcined samples were treated in air at 673 K for 4 h.

Specimens for spectroscopic analysis were prepared by deposition of a known amount of powder on a membrane (Nucleopore, thickness 10 μm, diameter 1.5 cm), in such a way as to obtain an absorption $\mu x \approx 2$ just above the edge. The absence of defects as fractures in the specimens and their uniformity was checked optically at a magnitude of 140×.

Measurements were carried out at the EXAFS-III station mounted on DCI (1.85

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0021-9517/90 $3.00

TABLE 1

Reference and Catalyst Samples

Sample	P/V ratio	Treatment temp (K)	Analysed	
			Pre-edge	EXAFS
$VO(acac)_2$	—	—	Y	Y
VO_2[a]	—	—	Y	N
V_2O_5	—	—	Y	Y
1	0.98	423	Y	Y
2	1.12	423	Y	Y
3	1.25	423	Y	Y
4	1.28	423	Y	Y
5	0.93	673	Y	Y
6	0.98	673	Y	Y
7	1.12	673	Y	Y
8	1.25	673	Y	N
9	1.28	673	Y	Y

Note. Y, yes; N, no.
[a] Data from Bianconi *et al.* (7).

TABLE 2

Assigned Values of E_0

Sample	E_0(eV)
$VO(acac)_2$	5479
V_2O_5	5478
1	5475
2	5475
3	5475
4	5475
5	5475
6	5475
7	5475
9	5475

GeV, 250 mÅ) at LURE, Orsay, using a double crystal Si(311) monochromator and two ionization chambers filled with He/Ne gas mixture. The spectral ranges 5250–6250 eV (ΔE = 2.0 eV) and 5445–5505 eV (ΔE = 0.3 eV) were scanned. Each energy was measured for 1 s and each spectrum was repeated three times. In Table 1 both catalyst and reference samples are summarized.

The EXAFS data processing was carried out on a Univac 1100/72 computer following our standard procedures (*4*), briefly summarized as follows. The background contribution $\mu_B(k)$ originating from the pre-edge region was extrapolated using a Victoreen relationship, then subtracted from the experimental data. The smooth atom-like contribution $\mu_0(k)$ was obtained by a 4th-order polynomial fit. The edge energy E_0 was arbitrarily chosen at the edge inflection. Values assigned to the various parameters are collected in Table 2. The EXAFS spectra multiplied by a cubic k factor were then Fourier transformed (FT) in the 3- to 13.5-$Å^{-1}$ range after application of a Gaussian window. After FT, the contribution of each atomic shell surrounding the absorbing atom could be isolated in the R space.

3. RESULTS

Pre-edge Region

The absorption spectra in the pre-edge region of samples treated at 423 K are reported in Fig. 1, together with those of some reference compounds. Spectra of the

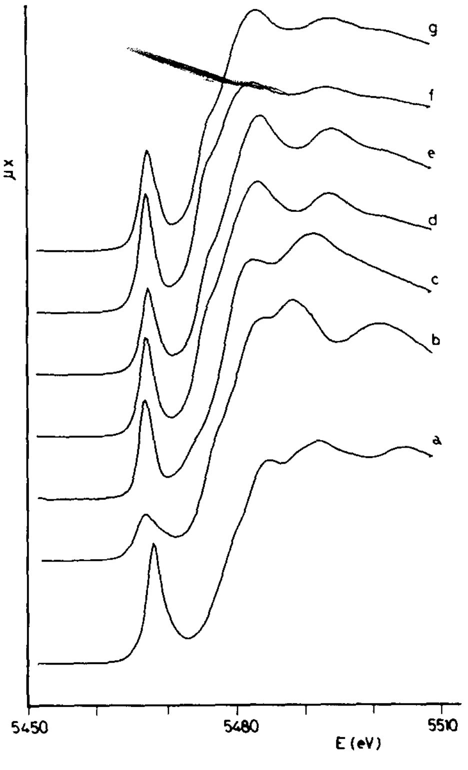

FIG. 1. Edge region of V_2O_5, VO_2, $VO(acac)_2$, and Samples 1, 2, 3, and 4 (from a to g, respectively).

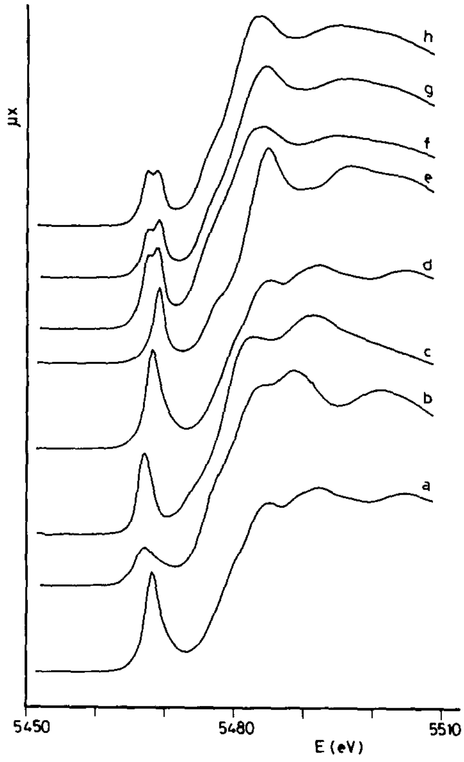

FIG. 2. Edge region of V_2O_5, VO_2, $VO(acac)_2$, and Samples 5, 6, 7, 8, and 9 (from a to h, respectively).

same samples after calcination at 673 K are reported in Fig. 2. The absorption scale of each spectrum has been normalized assuming 1 as the maximum energy value of the absorption continuum (in the EXAFS region, at $E = 5505$ eV, that is 30 eV above the threshold peak). The energy scale has been defined attributing the value of 5469 eV to the sharp maximum of the pre-edge absorption of V_2O_5 (*5*). A difference of about 1 eV is apparent among the values for the position of this peak (due to V^{5+}) and those of VO_2 and $VO(acac)_2$, where vanadium is present as V^{4+}.

The pre-edge vanadium peak has been attributed to the forbidden electron transition $1s \rightarrow 3d$ (*6*). Since it occurs only in systems where the octahedral coordination is distorted (*7, 8*), the transition can be used as a double indicator, both of the valence state and of the presence of a $1s$ symmetry around the absorber atom.

Since the pre-edge peak is always present (Figs. 1 and 2), vanadium must always be located in sites without a center of symmetry. Furthermore, from Fig. 1 it appears that in samples treated at 423 K vanadium is tetravalent. On the other hand, Fig. 2 shows that after treatment at 673 K some valence change occurs. More precisely, at low P/V ratios vanadium becomes pentavalent, while both V^{4+} and V^{5+} are present for P/V $\geq$ 1.12. In fact the pre-edge peak is clearly a doublet.

EXAFS Region

The EXAFS spectra of specimens dried at 423 K or calcined at 673 K are reported in Figs. 3 and 4, respectively. The corresponding FT moduli are reported in Figs. 5 and 6.

Provided that the amplitude backscattering factor $F_i(k)$ and the phase shift $\Phi_i(k)$ are

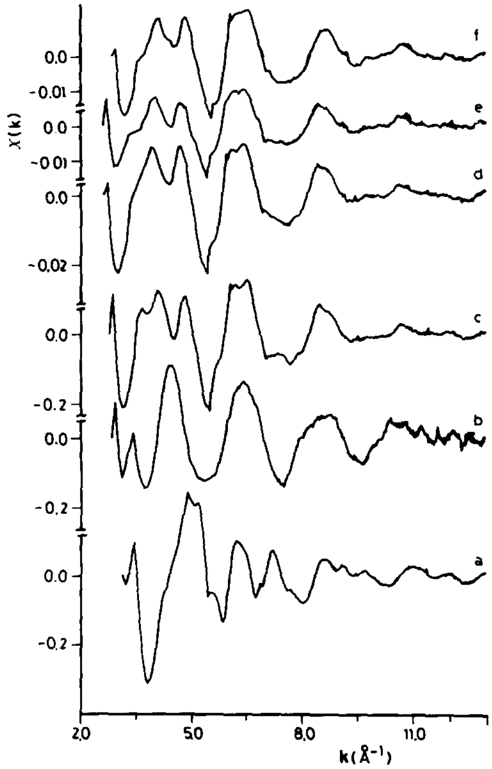

FIG. 3. EXAFS signal $\chi(k)$ vs k of V_2O_5, $VO(acac)_2$, and Samples 1, 2, 3, and 4 (from a to f, respectively).

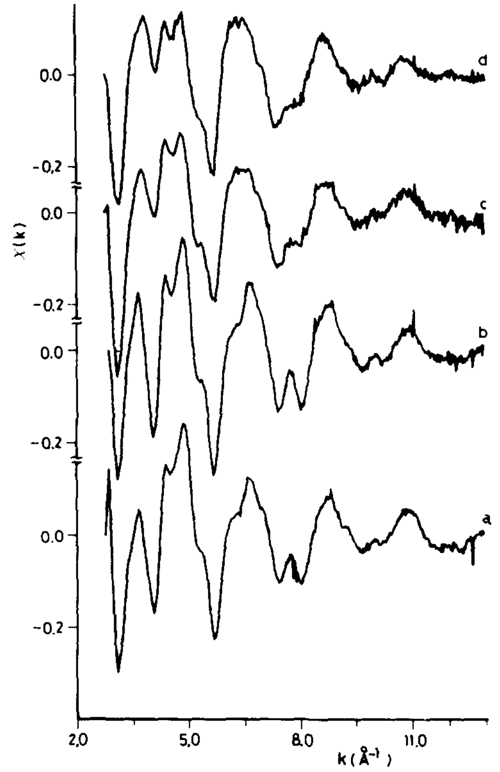

FIG. 4. EXAFS signal $\chi(k)$ vs k of Samples 5, 6, 7, and 9 (from a to d, respectively).

known, the structural parameters N_i (number of neighboring atoms defining the ith shell), R_i (average distance between the absorbing atom and the neighboring atoms), and σ_i (rms deviation) can be determined for a given sample. $F_i(k)$ and $\Phi_i(k)$ values can be experimentally obtained from suitable model compounds. Alternatively, values tabulated by Teo and Lee (*9*) can be used. We chose the latter course, checking the suitability of values on a compound having a known structure, namely VO(acac)$_2$, in which each V atom is surrounded by one oxygen atom at 1.58 Å and four more oxygen atoms at an average distance of 1.97 Å (*10*).

We parametrized the electron mean free path $\lambda(k)$ as proposed by Teo (11):

$$\lambda(k) = \frac{k}{\Gamma}.$$

The k-multiplied signal obtained anti-transforming the first FT peak of VO(acac)$_2$ was then rms-fitted between 4 and 10.75 A^{-1}. During fitting, coordination numbers were kept fixed at their crystallographic values, while k was free to vary following the relationship

$$k^1 = (k^2 + 0.2624E_0)^{1/2}.$$

In this way, Γ, R, and σ were determined. The final fit is reported in Fig. 7, while numerical values are collected in Table 3. The comparison with crystallographic data is satisfactory. For Γ, a value of 1.40 A^{-2} was found, its reliability being checked in the fitting of the anti-transform of V$_2$O$_5$ FT. In this case both N and R were left free to vary. The values obtained are reported in Table 4, again showing a good agreement among EXAFS data and crystallographic parameters (*12*). The final fit is reported in Fig. 8.

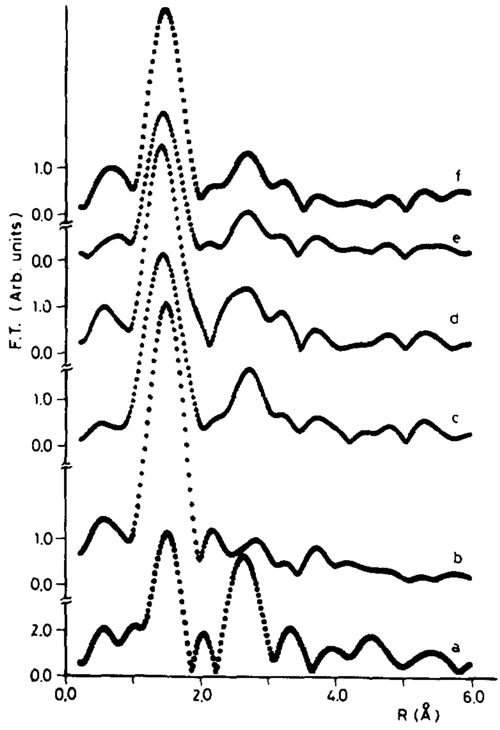

FIG. 5. Moduli of Fourier transform of V$_2$O$_5$, VO(acac)$_2$, and Samples 1, 2, 3, and 4 (from a to f, respectively).

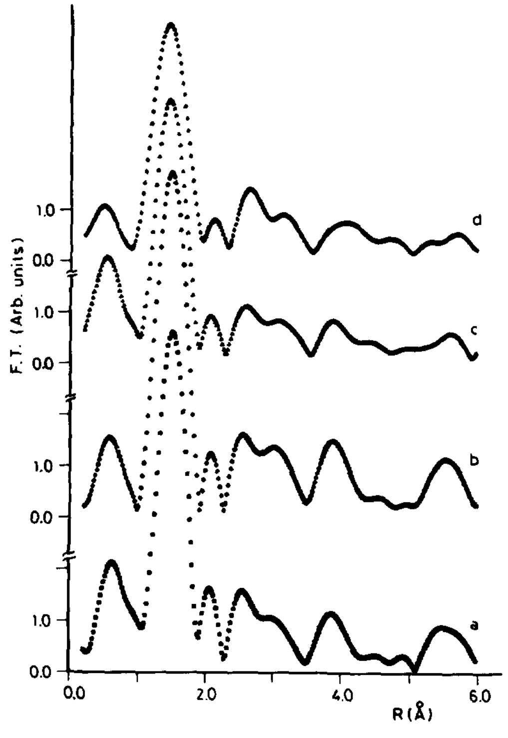

FIG. 6. Moduli of Fourier transform of Samples 5, 6, 7, and 9 (from a to d, respectively).

On catalyst samples, the fit was carried out on the signal obtained by anti-transforming the first peak of the FT. In the first instance, the hypothesis of only one V–O distance was assumed, leaving N, R, σ, and E free to vary. An acceptable agreement was never reached; thus two V–O distances were considered. In the latter case good fits were found, as shown in Fig. 9, concerning Sample 4. All other fits had the same quality, and the numerical results are collected in Table 5.

TABLE 3

Crystallographic Data and EXAFS Fit Results of VO(acac)$_2$

Crystallographic data V–O bond length (Å)	EXAFS results			
	N	R(Å)	σ(Å)	E(eV)
1.58	1.0	1.59	0.071	−19
1.98	4.0	1.98	0.059	−20

4. DISCUSSION

We first recall that, when considering the catalytic behaviour of a series of P–V catalysts having a P/V variable in a relatively narrow range around the value of 1, the most important feature is that the catalytic activity, specifically for the oxidation of n-butane to maleic anhydride, has a stepwise increase passing from a P-deficient situation to a P-excess situation. This was ob-

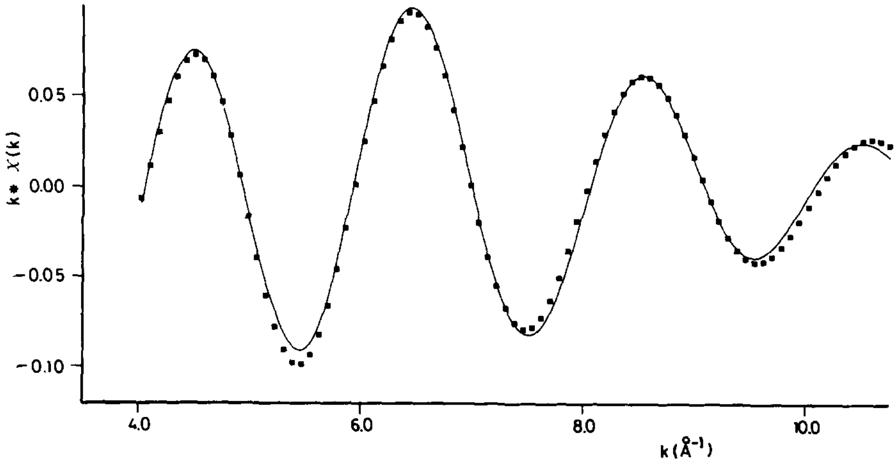

FIG. 7. Experimental signal (dotted line) and calculated signal (continuous line) of Sample VO(acac)$_2$.

TABLE 4

Crystallographic Data and EXAFS Fit Results of V_2O_5

	Shell			
	1	2	3	4
N				
a	1.0	1.0	2.0	1.0
b	1.0	1.1	2.1	0.9
V–O(Å)				
a	1.58	1.78	1.88	2.02
b	1.56	1.80	1.90	2.03
σ(Å)	0.075	0.081	0.070	0.095
Δ*E*(eV)	−21.	−21.	−20.	−19.

Note. a, crystallographic data; b, EXAFS results.

TABLE 5

EXAFS Fit Results of Catalyst Samples

Sample	*N*	*R*(Å)	σ(Å)	*E*(eV)
1	1.0	1.57	0.070	−20
	3.9	1.96	0.078	−15
2	1.1	1.56	0.072	−17
	3.8	1.97	0.074	−15
3	1.1	1.59	0.094	−20
	2.9	1.95	0.072	−15
4	1.0	1.58	0.090	−20
	3.1	1.95	0.055	−15
5	1.3	1.60	0.103	−20
	3.9	1.91	0.050	−14
6	1.4	1.57	0.090	−20
	4.0	1.92	0.049	−17
7	1.4	1.59	0.091	−20
	3.9	1.94	0.066	−14
9	1.4	1.59	0.080	−20
	4.2	1.96	0.078	−16

served by several authors (*13, 14*) and has been confirmed by us (*1*). In the attempt to interpret this sharp variation in catalytic activity, we performed several chemicophysical characterizations of the catalysts, considering both uncalcined (actually dried at 423 K) and calcined (at 673 K) samples. In our previous study no definitive answer was given. The EXAFS investigation of the P *K*-edge showed no particular variations of the phosphorus structural situation vs the P/V ratio. On the contrary, XPS showed some tendency for the oxidation properties to change. In fact, we observed that the temperature at which V^{4+} oxidized to V^{5+} increased on increasing the P/V ratio (*1*). This result agrees with the suggestion that an excess of phosphorus prevents the complete oxidation of vanadium by calcination in air, thus allowing the formation of the so-called β phase, considered the active phase (*15*).

Such a result, however, should be again

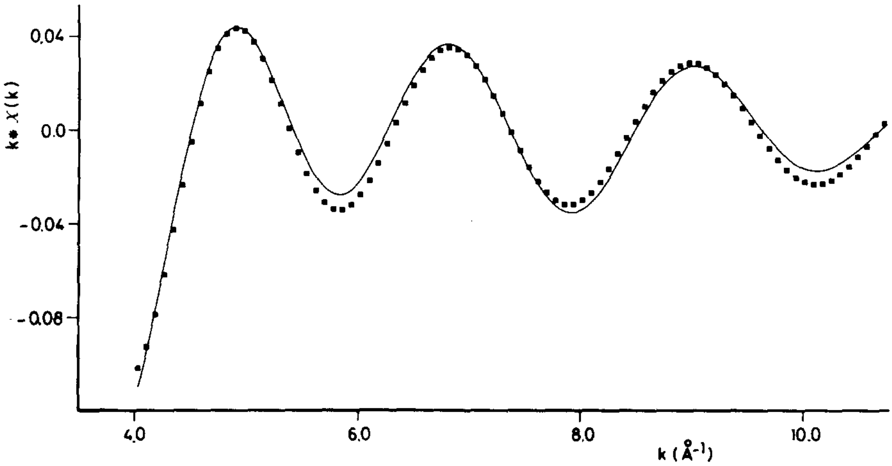

FIG. 8. Experimental signal (dotted line) and calculated signal (continuous line) of Sample V_2O_5.

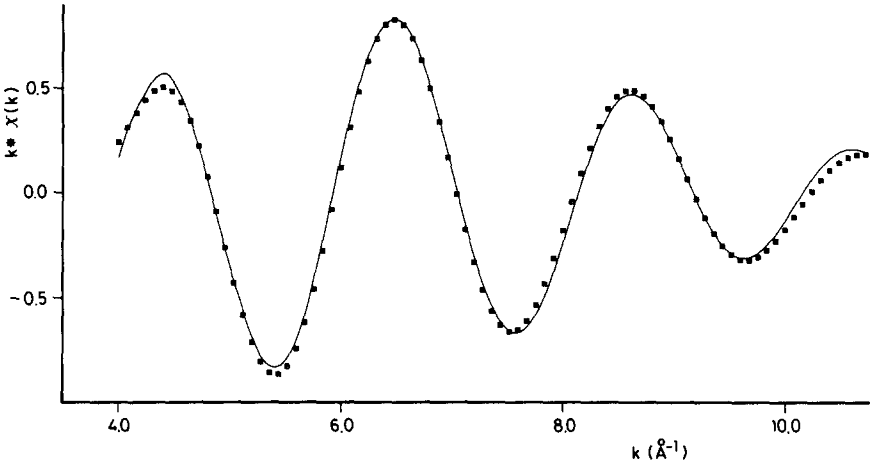

FIG. 9. Experimental signal (dotted line) and calculated signal (continuous line) of Sample 4.

considered a *consequence* of the composition variation, exactly like the catalytic activity, and not a *cause*. The fact that vanadium is involved in this behaviour prompted us to deepen the structural investigation concerning this atom, through the EXAFS investigation reported here.

Both pre-edge investigation and EXAFS measurements confirmed that variations in the structural situation of V do occur upon changing the catalyst composition. When the pre-edge peak was examined, interesting information was obtained on the actual valence state of vanadium before and after calcination and on its tendency to oxidize. For $P/V > 1$, the presence of the phosphorus excess seems to play a role in the incomplete oxidation to the highest valence state, that is, V^{5+}. Results obtained in the previous work (*1*) must be recalled in order to have a complete picture. XPS data are in full agreement with the present pre-edge result, suggesting that what we observed was a bulk phenomenon with an influence on the surface properties.

Also the XRD results then obtained on dried samples, that is, the occurrence of vanadium in a tetravalent state, agree with this work; in fact we mainly observed the presence of crystalline phases such as the so-called precursor of phase β (*15*) and, for $P/V > 1$, $VO(H_2PO_4)_2$.

EXAFS results suggest that more subtle variations occur by changing chemical composition of the catalysts. From Table 5, we can compare structural parameters of the uncalcined samples, structural parameters of calcined samples, and finally thermal treatment effects on the same sample.

At low P content, vanadium before calcination tends to coordinate five oxygen atoms, one at short distance (1.57 ± 0.02 Å) and four at long distance (1.96 ± 0.01 Å). While these distances do not vary with composition, in the presence of a phosphorus excess the coordination number decreases from 5 (that is 1 + 4) to 4 (that is 1 + 3). The thermal treatment does not cause variations in the population relative to the longest distance, while the shortest distance is in all cases populated by a number of oxygen atoms which exceeds 1 (more precisely, 1.4 ± 0.1). In its turn the total coordination number slightly exceeds 5 (5.4 ± 0.2).

It is likely that a fraction of V atoms come in a distorted octahedral coordination, while a majority remain in a square pyramidal coordination. This feature, however, is unlikely to be related to the activity variations, occurring in all samples regardless of chemical composition.

For calcined samples, an interesting structural variation occurs on increasing the P/V ratio; that is the V–O longest distance increases from 1.91 Å (shorter than that in uncalcined samples) to 1.96 Å, similar to that found in uncalcined samples. Even though the variation is small, it must be considered larger than the estimated error, taking into account that this distance is the more populated, so contributing in a substantial way to determine the frequency of the EXAFS oscillation. Our data do not allow us to state whether the distance variation is gradual with P/V or stepwise; however, stepwise variation would account better for the catalytic activity behaviour, together with the ability of vanadium to be present in the same specimen both as V^{4+} and V^{5+}. The EXAFS data here are related to a multiphase system, intrinsically inhomogeneous, so giving average results. Our study suggests that a deeper view of the catalysts could be achieved by a local microstructural technique, such as scanning transmission electron microscopy.

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