

Reactivity of some vanadium oxides: An EPR and XRD study

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Received 29 November 2004; received in revised form 2 February 2005; accepted 25 February 2005

Available online 25 March 2005

Abstract

V_2O_5 , VO_2 and V_2O_3 fresh samples and at different times after purchase or preparation (aged samples) were investigated by chemical analysis, redox treatments, XRD and EPR. The ageing process through a reaction with water and oxygen slowly oxidize crystalline VO_2 and V_2O_3 , leading to a quasi-amorphous phase with bariandite structure ($V_{10}O_{24} \cdot 12H_2O$). The role of water is the progressive demolition of the compact structures and formation of hydrated phase. Kinetic study of VO_2 oxidation by O_2 and $O_2 + H_2O$ mixture indicates that increasing the temperature up to 723 K the effect of water becomes less important. The reaction leads to partially oxidized products with decreasing water content: bariandite at room temperature, $V_3O_7 \cdot H_2O$ at 383 K and V_3O_7 at 723 K. Kinetic investigation of V_2O_5 reduction by CO at 633–723 K showed that the reduction process proceeds through the formation of V^{4+} and of electrons delocalized in the conduction band.

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Keywords: EPR of vanadium oxides; XRD of vanadium oxides; Reactivity of vanadium oxides

1. Introduction

Pure or supported vanadium oxides, are used in industrial processes, as catalysts in oxidation reactions to obtain important chemicals and reduction of environmental pollution [1]. Many papers have centered on the characterization of vanadium-based catalysts. The vanadium oxides exist in a range of single and mixed valency states (V^{5+} , V^{4+} , V^{3+} and V^{2+}) with a large variety of structures. Successful characterization therefore requires a multi-technique approach. These studies specified that the active sites are primarily redox sites [2,3].

Some years ago we characterized VO_x/ZrO_2 (ZV) catalysts by electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS) and redox cycles with CO and O_2 [4]. Depending on the reduction degree XPS disclosed the presence of V^{5+} , V^{4+} and V^{3+} . EPR detected two types of V^{4+} species: an isolated mono-nuclear species yielding signal with a well resolved

hyperfine structure and a clustered species (magnetically interacting V^{4+} in polyoxovanadate) yielding a single symmetrical line at $g = 1.96$ (peak-to-peak linewidth, $\Delta H_{pp} \approx 300$ G). Their relative abundance depended on V loading and on the reduction degree.

In VO_x supported on TiO_2 , Al_2O_3 , SiO_2 EPR investigation indicated that in concentrated samples, a symmetrical line similar to that found in ZV, underlay the hyperfine structure of isolated V^{4+} [5–7]. Even if the spectrum consisted mainly of the single line, the researchers mainly focused on the hyperfine structure of the isolated V^{4+} signal and attempted no quantitative evaluation.

A similar spectrum was detected also in pure non-stoichiometric V_2O_5 , prepared by various methods [8–10]. Hence this signal is typical of magnetically interacting V^{4+} in partially reduced V_2O_5 . Because adsorption of oxygen or air exposure at RT left the spectrum unchanged, V^{4+} species must be located in the bulk.

More extensive reduction of V_2O_5 yields many crystalline vanadium oxides [11,12]. Limiting the analysis to oxides with an average vanadium oxidation

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number between +5 and +4 (VO_n with $2.5 \geq n \geq 2$) the known ones are: V_2O_5 , V_3O_7 , V_4O_9 , V_6O_{13} and VO_2 . These oxides have been characterized by several spectroscopic techniques, but few EPR studies were published [13–15], probably because, except V_2O_5 and V_3O_7 , VO_n at RT are antiferromagnetic [11] and under some conditions are good electrical conductors. One of the most studied is VO_2 , a vanadium oxide that has a distorted rutile structure (monocline; space group $P2_1/c$) and a relatively high Néel temperature ($T_N = 345$ K). At T_N monoclinic VO_2 becomes tetragonal (undistorted rutile structure; space group $P4_2/mmm$) and because of transition from semiconductor to metallic state VO_2 electrical conductivity increases [16,17]. At $T < T_N$ VO_2 should therefore be EPR silent and at $T > T_N$, its high conductivity hinders resonant cavity tuning making it impossible to record the spectrum.

In our ZV characterization [4] we used commercial VO_2 as a reference for XPS measurements. The specimen, showing X-ray diffraction (XRD) pattern of the pure phase, yielded at RT an unexpected EPR spectrum consisting of a single symmetrical line ($g = 1.96$). At that time we did not further investigate this sample. About 2 years later we noticed by chance that the same VO_2 powder, kept closed in the manufacturer's bottle and opened without particular precautions only for drafts, had transformed into a hard and compact mass. The intensity of the EPR V^{4+} signal increased by a factor ten and the intensity of XRD peaks decreased by a factor four, indicating loss of crystallinity. Because transformation of monoclinic into amorphous phase is impossible without external action, we concluded that the VO_2 powder had reacted slowly with air. In the extensive literature on vanadium oxides, we found no investigation on their reactivity with atmospheric agents.

In the present work we investigated by chemical analysis, redox treatments, XRD and EPR VO_n fresh samples and at various times after their purchase or preparation (aged samples). The study focused the importance and the reliability of quantitative EPR measurements on concentrated systems containing V^{4+} ions.

2. Experimental

2.1. Sample preparation

We investigated commercial reagent grade products: VO_2 purchased from Aldrich and from Across and V_2O_3 from Aldrich.

According to the preparation methods reported in literature [12,18–21] we prepared the following vanadium oxides: V_2O_5 , V_2O_3 , V_3O_7 , V_6O_{13} and VO_2 . Calcination of ammonium metavanadate (AMV, Fluka) in air at 823 K for 8 h yielded V_2O_5 . The reduction of

this sample in H_2 flow at 1073 K for 20 h yielded V_2O_3 . Mixture of V_2O_5 and V_2O_3 in the molar ratio 5:1 accurately ground, sealed under vacuum in silica tube and then heated at 823 K for 7 days gave V_3O_7 . Thermal treatment under vacuum at 923 K for 3 days of V_2O_5 and V_2O_3 mixture in the molar ratio 2:1 yielded V_6O_{13} and in the molar ratio 1:1 VO_2 .

These preparation methods yielded specimens of low surface area ($2\text{--}3\text{ m}^2\text{ g}^{-1}$). The VO_2 specimen of higher surface area ($35\text{ m}^2\text{ g}^{-1}$) was prepared from decomposition at 723 K of the VO-complex, $(\text{NH}_4)_5[(\text{VO})_6(\text{CO}_3)_4(\text{OH})_9] \cdot 10\text{H}_2\text{O}$, under an N_2 flow at atmospheric pressure [22–24].

2.2. Chemical analysis

Because heating at 823 K in air for 24 h oxidized both VO_2 and V_2O_3 to V_2O_5 (XRD evidence), we evaluated their total vanadium content from the change in their weights between RT and 823 K. In the same oxides the weight loss after heating at 383 K in air for 24 h gave a rough evaluation of the amount of water adsorbed.

In both VO_2 and V_2O_3 chemical analysis yielded the concentration of vanadium in an oxidation state (o.s.) lower than 5. The samples were dissolved in concentrated (1:1) H_2SO_4 and titrated with KMnO_4 0.1 N.

2.3. Redox treatments

VO_2 fresh samples were submitted to oxidation treatments from RT to 723 K in pure O_2 (≈ 100 Torr) and in an $\text{O}_2 + \text{H}_2\text{O}$ mixture (≈ 100 Torr with constant $p_{\text{H}_2\text{O}} = 4.58$ Torr). Before each oxidation run the sample was evacuated at 723 K for 1 h.

V_2O_5 was submitted to reduction treatments from 503 to 723 K in CO (≈ 100 Torr). Before each reduction, the sample was re-oxidized with O_2 at 773 K for 1 h, followed by vacuum treatment at 473 K.

Samples underwent redox treatment in a circulating all-glass apparatus, connected to a high vacuum line. The apparatus was equipped with a magnetically driven pump, a pressure transducer (10^{-2} –1000 Torr, MKS Baratron) and a trap placed upstream from the reactor and kept at 77 K during the runs in O_2 and in CO or at 273 K during the runs in $\text{O}_2 + \text{H}_2\text{O}$ mixture. The pressure decrease yielded the amount of O_2 consumed during oxidation and the amount of CO consumed during reduction. From these amounts we determined the electrons lost or acquired per V atom (e/V) with an accuracy of 0.001.

2.4. Characterization techniques

BET surface areas ($\text{SA}/\text{m}^2\text{ g}^{-1}$) were measured by Kr adsorption at 77 K.

XRD measurements were done with a Philips PW 1729 diffractometer (CuK α , Ni-filtered radiation) equipped with an IBM computer (software APD-Philips). We periodically checked the sensitivity by measuring both the position and intensity of the peak at $2\theta = 28.46$ of the silicium standard purchased from Philips.

EPR spectra were recorded at RT and for some samples at temperatures from 77 to 400 K on a Varian E-9 spectrometer (X-band), equipped with a temperature control unit (Bruker B-ST 100/700) and with an on-line computer for data treatment. The absolute concentration of the paramagnetic species was determined from the integrated area of the spectra recorded at RT, using as standard the Varian Strong Pitch, SP (5×10^{15} spin cm^{-1}). This secondary standard was accurately calibrated with a series of primary standards, including solid $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{VO}(\text{acac})_2$ [25]. The number of spin cm^{-1} , N , of sample 'a' and standard 'b', obeying the Curie law, are related by the equation:

$$N_a = N_b \frac{g_b}{g_a} \frac{S_b(S_b + 1)}{S_a(S_a + 1)} \frac{A_a}{A_b}, \quad (1)$$

where A are the integrated areas, normalized for instrumental conditions, g the average g -values and S the spin. N_a was then divided by the linear density (g cm^{-1}) of the powder in the EPR tube to yield the concentration of the paramagnetic species (spin g^{-1}). Considering all the possible experimental errors, we estimate that the accuracy of the EPR quantitative measurements is within $\pm 20\%$. The g -value was determined using as reference the sharp peak at $g = 2.0008$ of the E_1' centre, formed by UV irradiation of the silica Dewar used as sample holder [26]. The lineshape was checked by measuring the width at half height, $\Delta H_{1/2}$, of the integrated signal and the peak-to-peak linewidth, ΔH_{pp} , of the first derivative signal. For a Lorentzian shape the ratio $\Delta H_{1/2}/\Delta H_{\text{pp}}$ is 1.73 [27]. We periodically checked the sensitivity of the spectrometer measuring both the amplitude and the integrated area of the SP reference standard.

3. Results and discussion

3.1. Fresh samples

XRD patterns of fresh VO_n , except VO_2 from VO-complex, showed sharp peaks, indicating well-crystallized phases (Fig. 1). The diffraction patterns were due to V_2O_5 (Fig. 1a), V_3O_7 (Fig. 1b), V_6O_{13} (Fig. 1c), VO_2 (Fig. 1d) and V_2O_3 (Fig. 1e) [28]. The VO_2 prepared at 723 K from VO-complex showed a broadening of XRD peaks.

Among the crystalline VO_n investigated, V_3O_7 alone yielded at RT an intense EPR spectrum consisting of a

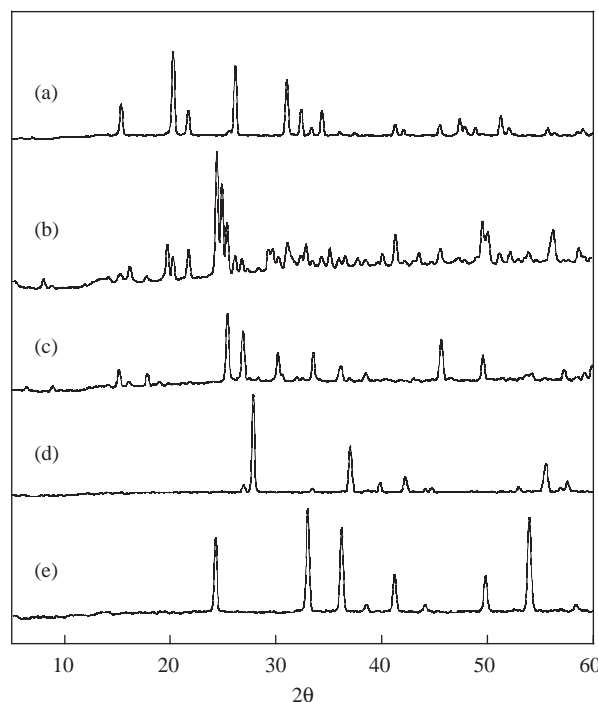


Fig. 1. XRD diffraction patterns of investigated vanadium oxides: (a) V_2O_5 , (b) V_3O_7 , (c) V_6O_{13} , (d) VO_2 , and (e) V_2O_3 .

single line of Lorentzian shape ($g = 1.96$ and $\Delta H_{\text{pp}} = 160$ G). In VO_2 this signal was very weak.

Because V^{5+} is diamagnetic and V^{3+} is EPR silent, V_2O_5 and V_2O_3 fresh samples yielded no signal. Because V_6O_{13} at 177 K has a phase transition [12] with an abrupt change in electrical conductivity [29], we could not tune the resonant spectrometer cavity and record the spectrum.

The VO-complex, used as precursor to prepare high surface area VO_2 , showed the same XRD pattern reported in literature [30] and an intense EPR single symmetrical line ($g = 1.965$ and $\Delta H_{\text{pp}} = 210$ G).

3.2. Reactivity of VO_n with air

Whereas aging at RT left the XRD and EPR spectra of V_2O_5 almost unchanged, it substantially altered those of VO_2 and V_2O_3 . After about 2 years of aging, in the XRD spectrum of commercial (Aldrich and Across) VO_2 samples, the sharp peaks due to the monoclinic phase decreased and weak, broad peaks appeared indicating the formation of a quasi-amorphous phase (compare Figs. 2a and b). After longer aging, we detected no sharp peak and the intensity of broad peaks increased (Fig. 2c). The broad peaks positions ($2\theta = 6.2$, 26 and 50) correspond to the most intense peaks of bariandite mineral, $\text{V}_{10}\text{O}_{24} \cdot 12\text{H}_2\text{O}$ [28]. When VO_2 aged samples were heated at 383 K in air the solid released most of the adsorbed water (see Section 3.3)

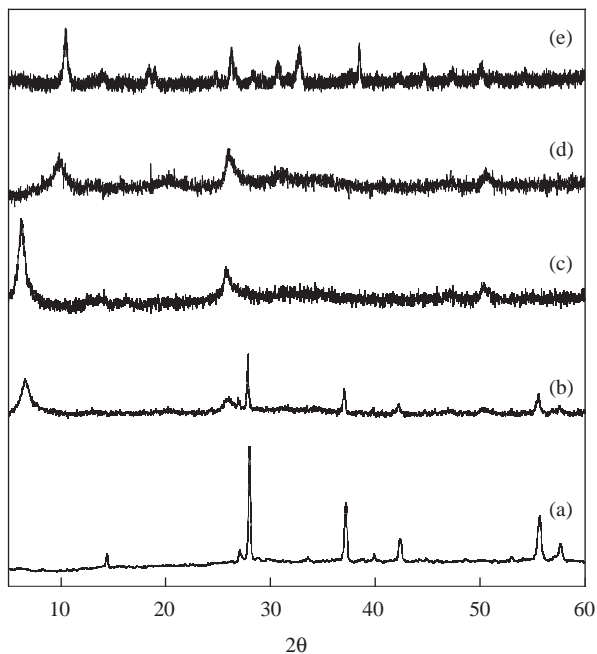


Fig. 2. XRD diffraction patterns of VO₂ (Aldrich): (a) fresh sample, (b) after 26 months, (c) after 95 months, (d) after 95 months and thermal treatment at 383 K in air, and (e) after 95 months and thermal treatment at 383 K in sealed glass tube.

and the first broad peak shifted from $2\theta = 6.2$ to 10 (compare Figs. 2c and d). Crystalline hydrated vanadium oxides (V₂O_{5- δ} ·nH₂O) have layered structures with different phases. Phase I, with a 14.2 Å spacing ($2\theta = 6.2$), is isostructural with bariandite. On dehydration consecutive phase transitions lead to phase I _{γ} , with a 8.3 Å spacing ($2\theta = 10.6$) [31–33]. When VO₂ aged samples were heated at 383 K in a sealed glass tube, their color turned from gray to green and the XRD pattern showed weak, sharp peaks of a new crystalline phase ($2\theta = 10.5, 26.3, 32.7$ and 38.4) (Fig. 2e). The sample color and the position of the XRD peaks corresponded to those of V₃O₇·H₂O [32].

After the same aging times (26 and 95 months) the weak EPR single line of the fresh VO₂ sample progressively increased in intensity (compare Figs. 3a with b and c).

The commercial V₂O₃ sample showed similar XRD and EPR spectral changes. After 95 months the XRD diffraction pattern of the fresh sample disappeared and weak, broad peaks of the quasi-amorphous phase with bariandite structure formed. At the same time EPR showed a single line similar to that of VO₂.

3.3. Quantitative evaluation of VO_n reactivity with air

Because the EPR spectrum of concentrated systems containing V⁴⁺ always consists of an exchange-narrowed symmetrical line of Lorentzian shape with $g =$

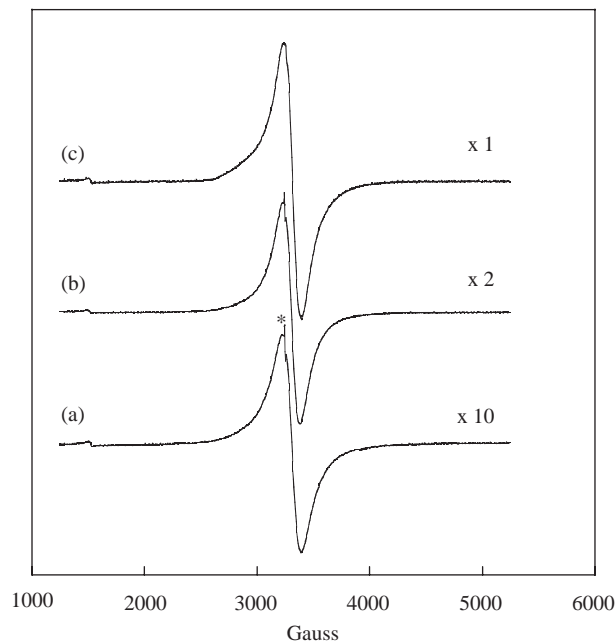


Fig. 3. EPR spectra recorded at RT on VO₂ (Aldrich): (a) fresh sample, (b) after 26 months, and (c) after 95 months. The asterisk indicates the marker at $g = 2.0008$ and the figure on each spectrum the relative gain.

1.94–1.96 and $\Delta H_{pp} = 100$ –300 G, the EPR parameters are of limited use in differentiating the various systems. The quantitative evaluation of the V⁴⁺ concentration is therefore essential for characterizing the solid. If the paramagnetic species obeys the Curie law, its concentration is reliably evaluated by Eq. (1). This is strictly true for isolated paramagnetic species. When the recording temperature (T) is much higher than $|\theta|$ (θ is the Curie–Weiss temperature, $\chi = C/(T - \theta)$) Eq. (1) is also applicable for interacting species in concentrated systems. Compounds that satisfy this requirement include some vanadyl salts or complexes [31] and crystalline or amorphous systems such as vanadium phosphate glasses [34].

Among crystalline VO_n oxides, Eq. (1) can be used to evaluate the concentration of V⁴⁺ in V₃O₇ because this oxide has a low $|\theta|$ value ($\theta < 0$, $|\theta| = 20$ K), determined by magnetic susceptibility measurements [12,20]. In our V₃O₇ specimen, Eq. (1) yielded a V⁴⁺ content equal to 16.5 wt%, corresponding to 86% of the nominal content calculated with the V⁴⁺V⁵⁺O₇ formula [22]. Similarly, for the VO-complex, used to prepare VO₂, Eq. (1) gave a V⁴⁺ content corresponding to 85% of the nominal content. In a sample of known composition, when the EPR concentration of the paramagnetic species corresponds to its nominal content ($\pm 20\%$), the correspondence indicates the reliability of Eq. (1).

To verify whether Eq. (1) was reliable for evaluating the V⁴⁺ content of VO₂ samples, we recorded at various

temperatures from 77 to 473 K the single line of the aged specimen and the signal of the standard SP. The plot $1/A$ vs. T shows that both the samples obey the Curie–Weiss law having low θ values ($\theta < 0$, $|\theta| < 10$ K) (Fig. 4). We therefore used Eq. (1) to determine the V^{4+} content detected by EPR in VO_2 specimens ($[V^{4+}]_{EPR}$ in Table 1).

In the same specimens the intensity decrease in the principal XRD peaks ($2\theta = 28.0, 37.1$ and 55.5) yielded the percentage of the monoclinic phase reacted with air (VO_2 reacted), and the intensity of the broad peak at $2\theta = 26$ roughly evaluated the quasi-amorphous phase amount (Table 1). At increasing aging time, in commercial (Aldrich and Across) samples the percen-

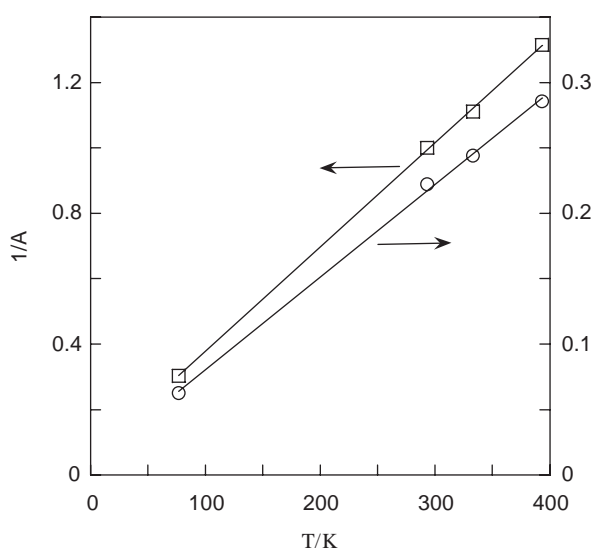


Fig. 4. Reciprocal of integrated area of EPR spectrum ($1/A$) vs. temperature: aged VO_2 (Aldrich) sample (\circ), and Varian Strong Pitch (\square).

tage of VO_2 reacted increased together with both the amount of the quasi-amorphous phase and $[V^{4+}]_{EPR}$.

Comparison between commercial samples with those from our preparation showed that during aging the reaction rate markedly depends on the sample surface area. After 3 months of aging, the VO_2 specimen with the highest surface area (prepared from the VO-complex) showed an increase of both VO_2 reacted and $[V^{4+}]_{EPR}$ comparable to that of commercial samples aged for longer times. By contrast, after 3 months the VO_2 specimen (prepared from V_2O_5 and V_2O_3 mixture) with a surface area similar to that of commercial samples showed very small changes (Table 1). Aging induced the fastest reaction on the specimen with the highest surface area.

Quantitative XRD and EPR measurements indicated that the aging-induced reaction took place on the surface of monoclinic VO_2 : the crystalline oxide transformed into quasi-amorphous hydrated vanadium oxide with bariandite structure and at the same time the V^{4+} amount detected by EPR increased. Because pure crystalline VO_2 must be EPR silent, as confirmed by the negligible $[V^{4+}]_{EPR}$ in the sample prepared from V_2O_5 and V_2O_3 mixture, we assign the EPR single Lorentzian line to magnetically interacting V^{4+} ions present in the quasi-amorphous phase formed during aging.

In VO_2 and V_2O_3 specimens comparison of $[V^{4+}]_{EPR}$ with analytical data (the V^{4+} content determined by titration and the total V-content determined by the weight change after calcination at 873 K) yielded additional information on the aging process (Table 2). Fresh VO_2 yielded a weight increase after calcination at 823 K, but the experimental value was lower than the calculated one for its oxidation to V_2O_5 (7.7 vs. 9.65 wt%). The V^{4+} content determined by titration was also lower than the total V-content. After heating at

Table 1

VO_2 samples from different sources after different aging times: surface area, XRD diffractions intensity and V^{4+} content detected by EPR

Source	SA ($m^2 g^{-1}$)	Aging time (months)	XRD		EPR
			VO_2 reacted (%)	Broad peak ^a (a.u.)	$[V^{4+}]_{EPR}$ (wt%)
Aldrich	3.2	Fresh	0	0	0.6
		26	77	56	3.9
		95	100	110	7.3
Across	2.7	Fresh	0	0	0.6
		29	53	80	
		50	100	115	8.4
Our preparation ^b	2.4	Fresh	0	0	0.1
		3	0	0	0.2
Our preparation ^c	35	Fresh	0	0	0.8
		3	47	0	4.0

^aIntensity of the broad peak at $2\theta = 26$, due to bariandite mineral.

^bFrom a mixture of V_2O_5 and V_2O_3 in the molar ratio 1:1 heated under vacuum at 923 K for 72 h.

^cFrom decomposition at 723 K for 5 h of vanadyl-carbonate complex under an N_2 flow at atmospheric pressure.

Table 2
Analytical data of commercial VO₂ and V₂O₃ samples after different aging times

Sample	Source	Aging time (months)	Weight change (%)		V-content (wt%)		[V ⁴⁺] _{EPR} (wt%)
			383 K ^a	823 K ^a	V _{total} ^b	V ⁴⁺ ^c	
VO ₂	Across	Fresh	−0.4	+7.7	60.3	56.5	0.6
		50	−13.5	−14.6	47.8	7.6	8.4
	Aldrich	95	−14.6	−16.0	47.1	6.6	7.3
V ₂ O ₃	Aldrich	95	−11.0	−14.3	48.0	5.0	4.6

^aTemperature of the thermal treatment in air.

^bDetermined from the weight change at 823 K (ΔW), $V_{\text{total}} (\text{wt}\%) = (1 + \Delta W/100) \times (2M_{\text{V}}/M_{\text{V}_2\text{O}_5}) \times 100$, where M is the molecular weight.

^cDetermined by titration with KMnO₄.

383 K, the specimen showed a small weight loss due to water desorption and a low [V⁴⁺]_{EPR} value. These data suggest that the commercial samples we investigated partially reacted with atmospheric agents during their storage.

In contrast with the crystalline fresh VO₂ sample, the aged amorphous specimens showed high amount of adsorbed water, a weight loss after calcination at 823 K and a low V⁴⁺ content by titration. These results indicate that during aging the specimen oxidized to V⁵⁺. After the treatment in air at 383 K the weight loss almost matched the value found after the treatment at 823 K, suggesting that heating at 383 K caused most of the water to desorb without appreciable oxidation of V⁴⁺. The V⁴⁺ content determined by titration was in satisfactory agreement with V⁴⁺ detected by EPR.

The weight loss (18.03 wt%) and the V⁴⁺ content (9.18 wt%) calculated for bariandite approached the values measured in aged samples (columns 5 and 7 in Table 2). The agreement is satisfactory considering the quasi-amorphous and poorly homogeneous solid formed in aging.

The analytical data of aged V₂O₃ were similar to those of aged VO₂.

During aging at RT crystalline V₂O₃ and VO₂ adsorb water and oxidize transforming into a quasi-amorphous hydrated vanadium oxide with bariandite structure, which contains V⁵⁺ and magnetically interacting V⁴⁺ ions detected by EPR.

3.4. Kinetic of VO₂ oxidation by O₂ and O₂+H₂O mixture

Treatments in O₂ and in O₂+H₂O mixture at RT for 12 h and at 473 K for 5 h yielded no oxygen consumption.

At 573 and 628 K, the runs in O₂+H₂O mixture yielded higher e/V values than those measured in pure O₂ (Figs. 5a and b). At the highest temperature (723 K) the presence of water vapor had no effect (Fig. 5c).

Because the curves were linear, we calculated the oxidation rate from their slopes. Our results indicate that the effect of the water vapor on the reaction rate becomes increasingly important as the reaction temperature decreases. Even if quantitative extrapolation of the reaction rates at RT is probably unreliable because of the complexity and variability of the solid, the results accord with the reaction with air at RT over the years.

Oxygen at RT promptly oxidized the V⁴⁺ ions exposed on the surface, whereas bulk V⁴⁺ required higher oxidation temperature to increase the mobility of oxygen ions and permit re-arrangement in a new hydrated phase, having open structures with chain or layered frameworks.

XRD spectra of the sample heated at 723 K indicated VO₂ reacted equal to 39% for the run in O₂ and 31% for the run in O₂+H₂O mixture. Both spectra showed weak extra peaks at $2\theta = 24.5$ and 24.9 , corresponding to the most intense peaks of V₃O₇ phase [28].

EPR spectra of VO₂ oxidized samples showed the single line at $g = 1.96$, whose intensity progressively increased with the increasing oxidation temperature. At 723 K the [V⁴⁺]_{EPR} was 6.0 wt% for the run in O₂ and 5.2 wt% for the run in O₂+H₂O mixture. Assuming that EPR detected V⁴⁺ ions in the V₃O₇ phase (XRD evidence), their concentration corresponds to 36% of V₃O₇ formed in the O₂ run and 32% in the O₂+H₂O run. These data are in reasonable agreement with XRD quantitative evaluation of VO₂ reacted.

XRD and EPR therefore revealed that VO₂ oxidation at 723 K yielded no V₂O₅ but V₃O₇, which required e/V values equal to 2/3 of the VO₂ reacted.

3.5. Kinetics of V₂O₅ reduction by CO

The reduction treatment of V₂O₅ (SA = 4.2 m² g^{−1}) at 503 K for 1 h yielded no appreciable CO consumption and no EPR signal. The treatment at 633 K for 1 h gave a very small CO consumption ($e/V = 0.0078$) and a weak EPR single line. The magnetically interacting V⁴⁺ ions detected by EPR ([V⁴⁺]_{EPR} = 0.035 wt%)

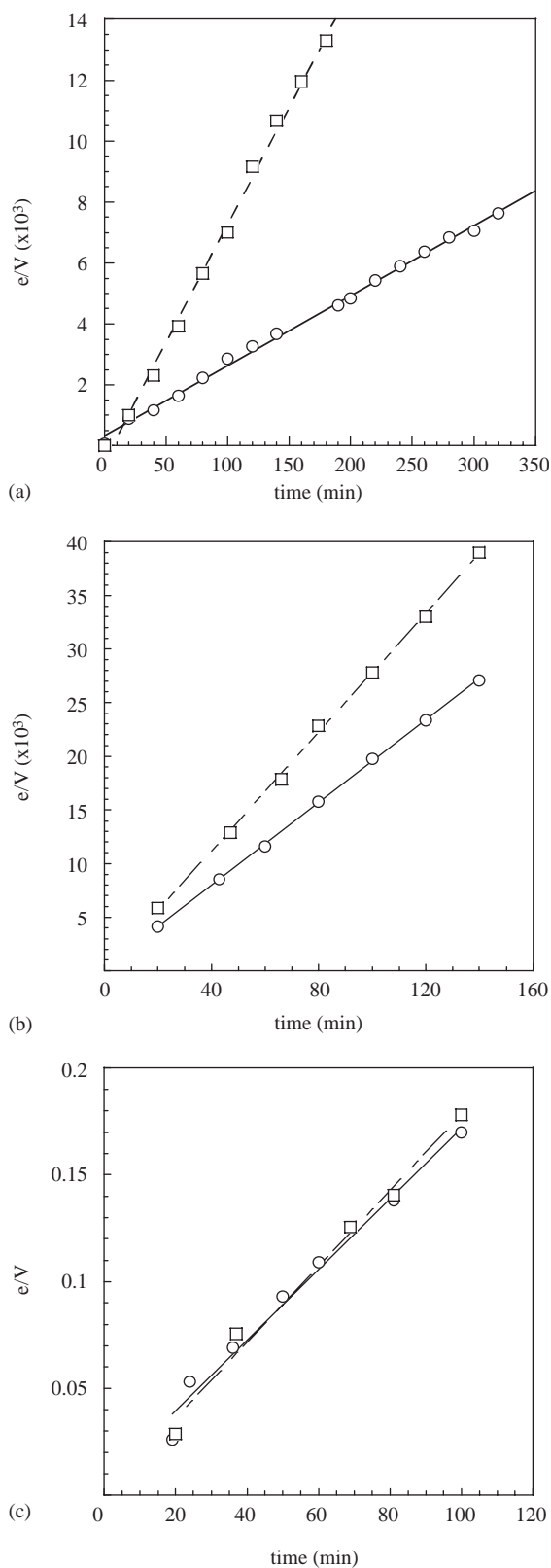


Fig. 5. VO_2 oxidation by O_2 (\circ) and $\text{O}_2 + \text{H}_2\text{O}$ (\square): e/V vs. time at 573 K (a), at 628 K (b), and at 723 K (c).

corresponded to 0.062% of the total V . The ratio between $[\text{V}^{4+}]_{\text{EPR}}/V$ and e/V ($[\text{V}^{4+}]_{\text{EPR}}/e = 0.00062/0.0078 = 0.08$) indicated that only a minute number of the electrons taken up by V_2O_5 caused the formation of EPR detectable species.

In the reduction at 773 K the e/V value increased almost linearly with time up to 5 h. By contrast, the intensity of the EPR signal was maximum at the first reduction stage and then decreased; therefore, increasing the reduction time, $[\text{V}^{4+}]_{\text{EPR}}/e$ strongly decreased (Fig. 6). We had difficulty in recording the EPR spectrum of the sample reduced for 5 h owing to phase inversion of the spectrometer and problems in cavity tuning; after a longer reduction time it became impossible to tune the cavity and to record the spectrum. As we had already found in other reduced oxides (TiO_2 , ZnO), this behavior is typical of conducting material. The exposure at RT of reduced V_2O_5 specimen to a small oxygen amount (20 Torr), yielding an adsorption under our detection limit, caused the recording difficulties to disappear and a single line with intensity similar to that after 5 h reduction time appeared.

Compared with VO_2 oxidation, V_2O_5 reduction by CO occurred at somewhat higher temperature. Non-stoichiometric V_2O_5 is an n -type semiconductor: vanadium ions in o.s. < 5 compensate the oxygen vacancies formed in the reduction process. Assuming that at least in the first reduction step the main process is $\text{V}^{5+} \rightarrow \text{V}^{4+}$, the semiconducting properties arise from a hopping process between V^{4+} and V^{5+} ions [27]. The above-mentioned problems in EPR recording (phase inversion, difficulty of tuning and effect of oxygen), the small values of $[\text{V}^{4+}]_{\text{EPR}}/e$ and its strong decrease with reduction time (Fig. 6), are consistent with the

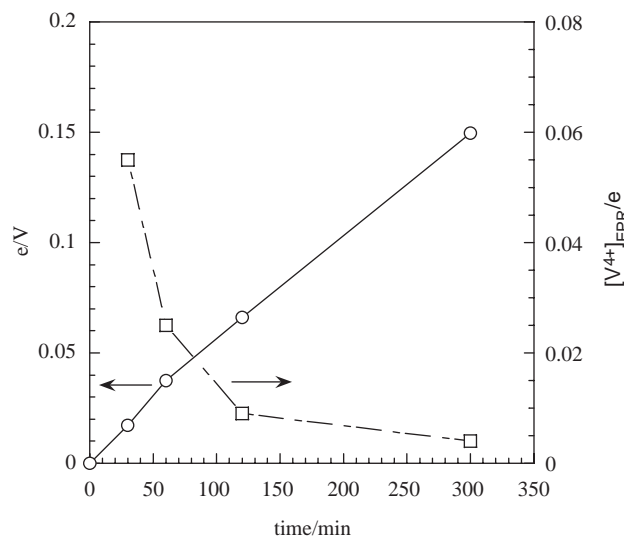


Fig. 6. Plot of V_2O_5 reduction by CO at 773 K: (\circ) e/V and (\square) $[\text{V}^{4+}]_{\text{EPR}}/e$ vs. time.

suggestion that most of the electrons acquired in the reduction process were delocalized in the conduction band.

A similar discrepancy between EPR and analytical data was found by others in non-stoichiometric $V_2O_{5-\delta}$ ($\delta = 0.07$) prepared by vacuum decomposition of AMV and explained with two consecutive reduction processes ($V^{5+} \rightarrow V^{4+} \rightarrow V^{3+}$) having two rate constants [9]. Moreover, they found that non-stoichiometric and stoichiometric V_2O_5 (obtained by heating $V_2O_{5-\delta}$ in oxygen at 573 K), submitted to reduction treatments with propylene, had the same dependence of the V^{4+} concentration detected by EPR vs. reduction time. In the run at the highest temperature (573 K) the V^{4+} detected by EPR had time dependence similar to that we found at 773 K.

Our results suggest that the two rate constants originate from the different formation rate of V^{4+} ions and of electrons delocalized in the conduction band.

4. Conclusions

Through a reaction with water and oxygen the aging at RT causes slow oxidation of crystalline VO_2 and V_2O_3 , leading to a quasi-amorphous phase with bariandite structure. The role of water is to hydrate the surface of the solid thus progressively demolishing the compact structures of the oxide and thereby forming hydrated phases, having open structures with chain or layered frameworks, in which the V^{4+} and V^{3+} ions are partially oxidized. In crystalline oxides surface hydration is wider at low temperature and is related to the acid–base properties of the surface.

As temperature increases, water vapor has a less important effect on the oxidation rate and oxidation leads to partially oxidized products with decreasing water content: hydrated vanadium oxide (bariandite) at RT and $V_3O_7 \cdot H_2O$ at 383 K. At 723 K, water vapor has no effect on the oxidation rate and oxidation produces V_3O_7 . Full oxidation to V_2O_5 requires a higher temperature, close to the melting point (963 K).

In concentrated V^{4+} systems the usefulness of EPR mainly resides in quantitative measurements. Quantitative EPR evaluation is reliable when the sample obeys the Curie law, namely in concentrated system when the absolute Curie–Weiss temperature value is much lower than the recording temperature. Quantitative data are less reliable for samples having mobile electrons and showing electric conductivity.

References

- [1] B.M. Weckhuysen, D.E. Keller, *Catal. Today* 78 (2003).
- [2] I.E. Wachs, L.E. Briand, J. Jehng, L. Burcham, X. Gao, *Catal. Today* 57 (2000) 323.
- [3] F. Trifirò, B. Grzybowska, *Appl. Catal. A (Special Issue)* 157 (1997).
- [4] M. Occhiuzzi, S. Tuti, D. Cordischi, R. Dragone, V. Indovina, *J. Chem. Soc. Faraday Trans. 92* (1996) 4337.
- [5] M.M. Kantcheva, V. Bushev, D. Klissurski, *J. Catal.* 145 (1994) 96.
- [6] J.G. Eon, R. Olier, J.C. Volta, *J. Catal.* 145 (1994) 318.
- [7] M. Che, B. Canosa, A.R. Gonzalez-Elipe, *J. Phys. Chem* 90 (1986) 618.
- [8] P. Tougne, A.P. Legrand, C. Sanchez, J. Livage, *J. Phys. Chem. Solids* 42 (1981) 101.
- [9] A. Bielanski, K. Dyrek, E. Serwicka, *J. Catal.* 66 (1980) 316.
- [10] E. Serwicka, *Z. Phys. Chem. N.F.* 67 (1990) 87.
- [11] K. Kosuge, T. Takada, S. Kachi, *J. Phys. Soc. Jpn.* 18 (1963) 318.
- [12] K. Kosuge, *J. Phys. Chem. Solids* 28 (1967) 1613.
- [13] S.M. Ariya, S. Ch. Akopyan, V. Vintruff, *Z. Anorg. Allg. Chem.* 352 (1967) 102.
- [14] O. Grossmann, N. Mattern, *Z. Anorg. Allg. Chem.* 432 (1977) 264.
- [15] A.V. Salker, *Indian J. Technol.* 27 (1989) 501.
- [16] K.D. Rogers, *Powder Diffr.* 8 (1993) 240.
- [17] F. Théobald, R. Cabala, J. Bernard, *J. Solid State Chem.* 17 (1976) 431.
- [18] S. Andersson, J. Galy, K.A. Wilhelmi, *Acta Chem. Scand.* 24 (1970) 1473.
- [19] K.A. Wilhelmi, K. Waltersson, L. Kihlberg, *Acta Chem. Scand.* 25 (1971) 2675.
- [20] K. Waltersson, B. Forslund, K.A. Wilhelmi, S. Andersson, J. Galy, *Acta Crystallogr. B* 30 (1974) 2644.
- [21] C. Lampe-Önnerud, J.O. Thomas, *Eur. J. Solid State Inorg. Chem.* 32 (1995) 293.
- [22] D. Labonnette, D. Tavel, *J. Chem. Res. (S)* (1984) 34.
- [23] C. Zheng, J. Zhang, G. Luo, J. Ye, M. Wu, *J. Mater. Sci.* 35 (2000) 3425.
- [24] C. Zheng, X. Zhang, J. Zhang, K. Liao, *J. Solid State Chem.* 156 (2001) 274.
- [25] D. Cordischi, M. Occhiuzzi, R. Dragone, *Appl. Magn. Reson.* 16 (1999) 427.
- [26] L.E. Halliburton, M.G. Jani, R.B. Bossoli, *Nucl. Instrum. Methods Phys. Res. B* 1 (1984) 192.
- [27] C.P. Poole Jr., *Electron Spin Resonance. A Comprehensive Treatise on Experimental Techniques*, Wiley-Interscience, New York, 1967, p. 798.
- [28] V_2O_5 : ASTM 89-2482; V_3O_7 : ASTM 71-0454; V_6O_{13} : ASTM 89-0100; VO_2 : ASTM 44-0252; V_2O_3 : ASTM 34-187; and $V_{10}O_{24} \cdot 12H_2O$: ASTM 25-1006.
- [29] S. Kachi, T. Takada, K. Kosuge, *J. Phys. Soc. Jpn.* 18 (1963) 1839.
- [30] T.C.W. Mak, P. Li, C. Zheng, K. Huang, *J. Chem. Soc. Chem. Commun.* (1986) 1597.
- [31] T. Yao, Y. Oka, N. Yamamoto, *J. Mater. Chem.* 2 (1992) 337.
- [32] T. Chirayil, P.Y. Zavalij, M.S. Whittingham, *Chem. Mater.* 10 (1998) 2629.
- [33] P.Y. Zavalij, M.S. Whittingham, *Acta Crystallogr. B* 55 (1999) 627.
- [34] L.I. Horváth, I. Geresdi, T. Szörényi, *J. Non-Cryst. Solids* 70 (1985) 429.