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Magnetic resonance study of $SbVO_5$ thermal decomposition products

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A new $SbVO_5$ compound, which can be synthesized from an equimolar mixture of Sb_2O_3/V_2O_5 or α-Sb_2O_4/V_2O_5 oxides by heating in air to temperatures below 650 °C, is stable in air up to 710 °C and in argon atmosphere up to ~645 °C. At higher temperatures it decomposes into a phase with a rutile-type structure. Using electron spin resonance (ESR) we have studied the magnetic properties of the thermal decomposition products of $SbVO_5$ in air (sample 1D) and in argon atmosphere (sample 2D), as well as two phases of the of the rutile-type structure (samples 3S and 4S) synthesized at conditions similar to the previous two samples. The ESR spectra of all four samples consisted mostly of two types of lines: a narrow line (designated as the N component) and a very broad line (designated as the VB component). Close inspection of the ESR parameters for these components allowed the samples to be grouped according to the environment they were annealed in (air or oxygen-free argon). The origin of these lines and the implications concerning the phase composition of the decomposition products are discussed. ESR results confirm that the solid decomposition product of $SbVO_5$ in air is a non-stoichiometric compound with a rutile structure and formula $Sb^{5+}_{0.9}V^{3+}_{0.1}V^{4+}_{0.8}\square_{0.2}O_4$ and in argon a near -stoichiometric $V^{4+}Sb^{5+}O_{4.5}$.

Key words: *electron spin resonance; vanadate compounds*

1. Introduction

Acrylonitrile (ACN), with a worldwide annual production of well over 5 million tons, is produced, among others, by the ammoxidation of propylene, using catalysts from the Bi-Fe-Mo-O or USb_3O_{10}–Sb_2O_4 (SOHIO process) systems [1, 2]. In the last decade, for economic reasons (the price of propylene is about six times higher than

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that of propane), investigations of new catalytic materials for the direct synthesis of acrylonitrile from propane have been carried out, which would reduce the price of ACN by ~20 % [3–6]. As the catalysts synthesized from a mixture of antimony and vanadium oxides and/or containing compounds formed in the Sb–V–O system reveal a good activity and high selectivity in the direct ammoxidation of propane to acrylonitrile, they have been the subjects of an intense research [4, 7–10].

Knowledge of the exact number of phases formed in the Sb–V–O system and of their chemical and physical properties is crucial for the formation of a new class of catalysts. According to rich literature on the possible phases formed in the Sb–V–O system, the most important two factors during synthesis are the type of starting oxides and the gaseous atmosphere used [11–14]. It has been established that the annealing of an equimolar mixture of Sb_2O_3/V_2O_5 or α-Sb_2O_4/V_2O_5 oxides in air at 800 °C leads to the formation of a non-stoichiometric compound with a rutile structure, described by the formula $Sb^{5+}_{0.92}V^{3+}_{0.28}V^{4+}_{0.64}\square_{0.16}O_4$ where the square denotes a cation vacancy [11–13]. Canovas et al. have synthesized vanadium antimonate from Sb_2O_3/V_2O_5 in an atmosphere with a variable O_2/N_2 ratio and obtained the first continuous series of non-stoichiometric rutile-type $Sb_{0.9}V_{0.9+x}\square_{0.2-x}O_4$ ($0 < x < 0.2$) phases containing variable proportions of V^{3+} and V^{4+} ions, ranging from $Sb^{5+}_{0.9}V^{3+}_{0.1}V^{4+}_{0.8}\square_{0.2}O_4$ ($x = 0$ in O_2) to $Sb^{5+}_{0.9}V^{3+}_{0.9}V^{4+}_{0.2}\square_{0.0}O_4$ ($x = 0.2$ in N_2) [12]. For the second series, synthesized at reducing conditions, the authors described the phases as $Sb_{0.9-y}V_{1.1+y}O_4$, where $0 < y < 0.7$. In compounds of this type, antimony – similarly as in the previous series – is in the 5+ oxidation state and vanadium in both the 3+ and 4+ oxidation states. This series of phases was recognized as a solid solution spreading between $Sb_{0.9}V_{1.1}O_4$ and VO_2 [12]. Birchal and Sleight [13], as well as Berry et al. [14], have synthesized vanadium antimonate from Sb_2O_3/V_2O_5 in closed containers at 800 °C and obtained $Sb_{0.95}V_{1.05}O_4$ and $VSb_{1-y}O_{4-2y}$ ($0 < y < 0.1$), respectively. Berry et al. have provided evidence that in an atmosphere of oxygen-free nitrogen the obtained compound could be described by the formula $VSb_{1-y}O_{4-3/2y}$ [14]. The opinion of the majority of researchers in this field is that antimony in these phases is in the 5+ oxidation state, while vanadium in 4+ one. A small number of researches claim that the stoichiometric $Sb^{3+}V^{5+}O_4$ could be synthesized from an equimolar mixture of antimony(III) oxide with vanadate(V) oxide in argon atmosphere [15–17]. Furthermore, near stoichiometric antimony vanadate, with the formula $V^{4+}Sb^{5+}O_{4.5}$, could be synthesized using a novel peroxide-based sol-gel synthesis procedure [18].

Our investigations have shown that annealing an equimolar mixture of Sb_2O_3/V_2O_5 or α-Sb_2O_4/V_2O_5 oxides at temperatures not higher than 650 °C leads to the formation of the $SbVO_5$ compound in air [19], and the $SbVO_{4.5}$ ($Sb_2V_2O_9$) compound has been synthesized from α-Sb_2O_4/V_2O_5 oxides in an atmosphere of oxygen-free argon [20].

$SbVO_5$ differs from currently known compounds in many ways: its XRD, IR, and thermal properties are different, not to mention its colour. It is very probable that in this compound the Sb and V ions are in the 5+ oxidation state [21]. $SbVO_5$ is stable in

air up to 710 °C, and in oxygen-free argon up to ~645 °C, where it decomposes in the solid state into one phase with a rutile-type structure [19].

Electron spin resonance (ESR) studies of the $SbVO_5$ compound have already been erformed in the 3.6–300 K temperature range [21]. At room temperature only a weak ESR signal was detected, corroborating the absence of bulk V(IV) ions in the structure. Below 100 K, a well resolved hyperfine structure typical of isolated vanadium ions in axial symmetry, present as VO^{2+} species, and a broad line attributed to electron hopping along V^{4+}–O–V^{5+} bonds, can be seen. At 3.65 K, a spectrum typical for a triplet state, indicating the presence of two interacting VO^{2+} species, was recorded.

In this paper, the results of ESR investigations of both decomposition products of $SbVO_5$ (in air and in argon) and of the rutile-type phases, synthesized in conditions similar to the decomposition conditions, have been carried out. The aim of this study is to gain knowledge on the decomposition products of $SbVO_5$ and to resolve the problem of the oxidation state of vanadium ions (+3 or +4) in these phases. The question of the oxidation states of metal ions in non-stoichiometric rutile-type compounds has been the subject of some controversy and is of great importance for the interpretation of catalytic mechanisms.

2. Experimental

$SbVO_5$ was prepared by heating an equimolar mixture of V_2O_5 (p.a. product, POCh, Gliwice, Poland) with α-Sb_2O_4 (obtained by heating in air pure Sb_2O_3, Merck, Germany, in air) by the method described in Ref. [19]. Two samples of the obtained $SbVO_5$ powder were subject to the following thermal treatment: the first sample (designated as 1D) was heated in air at 735 °C for 24 h, the second (designated as 2D) was heated in oxygen-free argon for 24 h at 660 °C. The heating temperatures were selected so as to fall into the temperature range between the onset and maximum temperatures of the endothermic effect recorded in the DTA curves of $SbVO_5$. These decomposition changes were accompanied by a mass loss of ~ 3.5 wt. % in air and 3.2 wt. % in argon, as evidenced by TG curves.

Two additional samples (designated as 3S and 4S) were obtained by heating an equimolar mixture of α-Sb_2O_4 and V_2O_5 oxides at temperatures close to that at which $SbVO_5$ decomposes. Sample 3S is a product of the synthesis of these oxides in air at 735 °C, lasting 36 h (2 times by 18 h). Sample 4S was synthesized in an oxygen-free argon atmosphere at 650 °C for 24 h. The diffractograms of all four samples were very similar and contained the same set of diffraction lines. The only difference was that the respectable interplane distances were slightly greater for samples synthesized in air. The indexation of a selected diffractogram showed that the investigated phases had a rutile-type structure [20].

ESR measurements were carried out on a standard X band spectrometer (Bruker E 500) at room temperature. The spectrometer was equipped with a TE_{102} cavity and 100 kHz field modulation. The investigated samples were in powder forms and were

placed into 4 mm diameter quartz tubes. The masses of samples 1D, 2D, 3S, and 4S were 30.7, 26.6, 56.0, and 47.0 mg, respectively. ESR detects the power P absorbed by the sample from the transverse magnetic microwave field as a function of the static magnetic field. The signal-to-noise ratio is improved by recording the derivative d*P*/d*H*, using the lock-in technique with field modulation. For the estimation of the number of spins participating in the resonance, a standard sample of polycrystalline $VOSO_4 \cdot 5\ H_2O$ was used.

3. Results and discussion

Vanadium ions exhibit a wide range of stable oxidation states, among them being the often-encountered V(III), V(IV), and V(V) states. Vanadium(V), with a $3d^0$ configuration, is diamagnetic and thus ESR inactive. Vanadium(III) is not a Kramer's ion, possessing two unpaired electrons, and as such is not likely to give an ESR signal in the experimental condition of the present study. In many biological and materials science systems the majority of vanadium exists in paramagnetic oxovanadium(IV) VO^{2+} ions complexed in some form. Various V(IV) species could be detected by the ESR technique. Vanadium (IV) clusters give rise to a broad signal owing to significant dipolar interactions, whereas isolated V(IV) species exhibit a hyperfine structure derived from the interaction of free electrons ($3d^1$) with the magnetic nuclear moment of ^{51}V (I = 7/2). In this case, the ESR signal splits eightfold. In solids, the hyperfine structure can be substantially suppressed or even disappear due to various interactions of electron spins with their surroundings. For example, in conducting vanadate glasses (V_2O_5–TeO_2) such interaction occurs via the so-called super-exchange of electrons, i.e. the hopping of a mobile electron along V^{4+}–O–V^{5+} bonds [22].

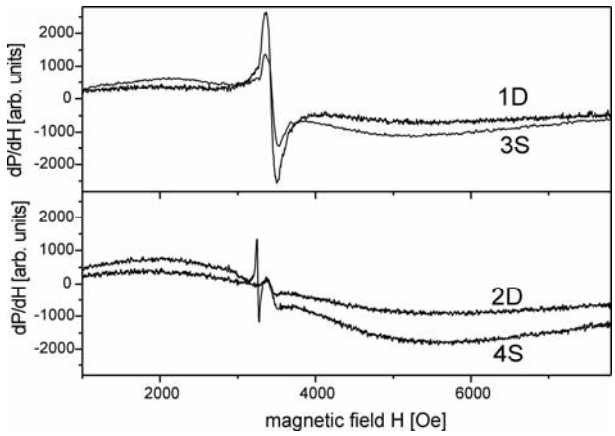

Fig. 1. ESR spectra of the four investigated samples:
samples 1D and 3S – upper panel, samples 2D and 4S – lower panel.
The sample masses are different, hence
the spectral intensities are not directly comparable

The experimental ESR spectra, taken at room temperature, of all four investigated samples are shown in Fig. 1. All recorded spectra show the same features: the presence of one very broad (designated as VB) and one relatively narrow (designated as N) resonance line. Additionally, the spectrum of sample 4S contains a very narrow component (designated as VN). The values of the ESR parameters for all these lines, i.e. the peak-to-peak linewidth ΔH_{pp}, effective g-factor, and relative intensity I_r, were found by fitting the experimental spectra and are presented in Table 1. As the linewidth of the VB component is of the same order of magnitude as the resonance field H_{res}, both circular components of the exciting linearly polarized microwave field have to be taken into account in calculations. Therefore, the resonance at the reversed magnetic field, $-H_{res}$, was included into the fit (using a Lorentzian-type line) for the VB component [23]. The relative intensity I_r was calculated by numerical integration of the absorption spectra of the four investigated samples and refers to a unit mass of the sample. The most intensive VB component in the ESR spectrum of sample 4S was taken as the unit of the relative intensity.

Table 1. ESR parameters for various spectral components of the four investigated samples

Sample	Spectrum component	Peak-to-peak linewidth [Oe]	Effective g-factor	Relative intensity [a. u.]
1D	VB	4160	1.880	0.59
	N	142	1.957	$30\cdot10^{-4}$
2D	VB	4650	1.868	0.92
	N	130	1.967	$4\cdot10^{-4}$
3S	VB	3780	1.912	0.47
	N	149	1.961	$30\cdot10^{-4}$
4S	VB	4480	1.877	1.00
	N	144	1.965	$7\cdot10^{-4}$
	VN	27	2.074	$0.7\cdot10^{-4}$

None of the observed lines displays the hyperfine structure expected for V^{4+} paramagnetic ions with nuclear spins. Usually, this absence is explained by the exchange interaction between neighbouring ions and by the delocalisation of the $3d^1$ electrons of V^{4+}, particularly in the conducting state of the material. It follows that in our samples there are no V^{4+} ions that are not subject to magnetic interactions. Thus the observed paramagnetic centres must be close enough ($d < 0.7$ nm) to allow spin–spin interactions. For the VB component, the interaction between V^{4+} ions is particularly strong, leading to the formation of bulk clusters. A similar broad line was observed in variable oxygen stoichiometry materials such as $La_2NiO_{4+\delta}$ and $(V_{1-x}Mo_x)_{2-\delta}O_3$ [23].

The relative intensity of the VB component in the four investigated samples (Table 1) allow them to be divided into two groups: those processed in oxygen-free argon and with larger intensity (samples 4S and 2D), and the second group processed in air

and exhibiting the ESR signal roughly twice as weak (samples 1D and 3S). Also, the linewidths and *g*-factors of the VB component correlate well with this division: samples processed in air are on average 595 Oe narrower than those processed in oxygen-free argon, and their *g*-factors are larger by 0.024.

Although the ESR intensity of the N component is about three orders of magnitude smaller than that of the VB line, the same grouping of samples is observed if the ESR intensity of the N spectral component is considered. This time, though, samples 1D and 3S display a larger intensity, and their integral intensity is about six times stronger than that of samples 2D and 4S. The linewidth (130–149 Oe) and *g*-factor (1.957–1.967) for this line seem to be independent of the type of sample. The VN component observed only in the spectrum of sample 4S is the weakest of all lines, about one order of magnitude less intensive than the weakest N component line. Its linewidth is small and its *g*-factor greater than 2 – it may arise from an unwanted paramagnetic contamination and will not be discussed further.

A comparison of the ESR intensities of the four samples with the intensity of a standard allows the absolute number of paramagnetic centres in the investigated compounds to be determined. Taking into account the uncertainties in determining the masses and areas under the ESR absorption curves, the accuracy of this number was estimated to be about 30%. Within this limit, it was calculated that almost all vanadium ions present in the samples contributed to the recorded ESR spectra, i.e. were in the 4+ oxidation state. It is known that the spectra of vanadium(IV) ions, located in a perfect oxygen octahedron, are characterized by a short spin-lattice relaxation time [24]. As a result, the ESR spectra of V(IV) ions in the substitution positions of rutile are observed only at low temperatures. In contrast, in the case of V(IV) ions in a pressed octahedron, and at the interstitial positions, ESR spectra are observed at room temperature.

Taking into account all the discussed ESR features of the investigated samples, it is proposed that the VB component lines arise from vanadium(IV) clusters present inside the micrograins forming the powder samples, while the B component arises from vanadium(IV) ions located on the surface of these grains. The relative ESR intensity of the VB and B components ($\sim 10^{-3}$) reflects the relative number of these centres and also the volume fraction of the sample they occupy. This value seems reasonable taking into account the mean grain diameter. As in the $SbVO_5$ compound, the bulk of the vanadium is in the 5+ valence state and thus unobservable in ESR spectrum, and the heating of this sample causes the conversion of V(V) to V(IV) and loss of oxygen. As the electrons needed for vanadium conversion originate from released oxygen, the bigger the oxygen loss the stronger the intensity of the ESR signal. This is indeed what is being observed: oxygen loss is bigger for samples heated in an argon atmosphere and the VB component in the ESR spectra of these samples is more intense. A slightly greater linewidth of the argon-processed samples might be evidence of a larger spread of the ESR parameters of the involved paramagnetic centres, which in turn could be interpreted as the result of a more defective environment.

As far as the B component of the ESR spectra is concerned, it is proposed that it originates from V(IV) ions located at or near the surfaces of the grains. There are relatively more such vanadium(IV) ions in oxygen-processed samples, as the availability of valence conversion electrons is greater in these samples. The mobility of such electrons might be significantly reduced due to the abundance of defects in this layer, leading to long relaxations and narrow ESR lines.

Similarly, the ESR spectra of samples 1D and 3S (both air-processed) allow the assumption that the solid decomposition product of $SbVO_5$ in air is a non-stoichiometric compound with a rutile structure and the formula $Sb^{5+}_{0.9}V^{3+}_{0.1}V^{4+}_{0.8}\square_{0.2}O_4$ [12]. This assumption is further corroborated by comparing the theoretical (3.52 wt. %) and experimental (3.5 wt. %) oxygen mass loss during the decomposition stage:

$$9SbVO_5 = 10Sb_{0.9}V^{3+}_{0.1}V^{4+}_{0.8}O_4 + 5/2O_2$$

Oxygen released during that process increases the partial pressure of the gas in air, which stimulates the increase of the number of cation vacancies in the crystal lattice. An investigation of the electrical properties of the decomposition product has showed that it is a p-type semiconductor [25]. Slight differences between the ESR spectra of samples 1D and 3S may be related to a lower concentration of cation vacancies in sample 3S. According to literature data, the formula for the 3S compound is $Sb^{5+}_{0.92}V^{3+}_{0.28}V^{4+}_{0.64}\square_{0.16}O_4$. Thus the V^{4+}/V^{3+} ratio for the sample 1D should be significantly greater than that for 3S. This is indeed what can be observed for the ESR intensity of the VB component in these samples.

The solid decomposition product of $SbVO_5$ in oxygen-free argon is probably the near stoichiometric compound $Sb^{5+}V^{4+}O_{4.5}$. Its formation is favoured by a lower temperature of decomposition and a lower oxygen partial pressure, which results in the lack of that gas at the solid/gas interface. Thus the decomposition process could be summarized by the equation

$$SbVO_5 = Sb^{5+}V^{4+}O_{4.5} + 1/4O_2$$

Mass loss calculated from this equation (3.17 wt. %) compares favourably with the value observed using thermogravimetric methods (3.2 wt. %).

4. Conclusion

Two decomposed samples of $SbVO_5$ and two synthesized samples aimed at obtaining the same compounds were investigated by room temperature ESR. The obtained spectra were similar, proving that decomposition and synthesis leads to the same results. The oxidation state of the majority of vanadium ions has been determined as 4+. The ESR spectra of two types of vanadium paramagnetic centres have been identified in the investigated samples and connected with the surface and interior of the grains.

ESR results confirm that the solid decomposition product of $SbVO_5$ in air is a non-stoichiometric compound with a rutile structure and formula $Sb^{5+}_{0.9}V^{3+}_{0.1}V^{4+}_{0.8}\square_{0.2}O_4$, and in argon the near stoichiometric $V^{4+}Sb^{5+}O_{4.5}$. An investigation of the temperature dependence of the ESR spectra may shed more light on the origin and dynamics of the paramagnetic centres and is planned for the future.

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