

EPR study of vanadium-loaded yttrium-cerium-zirconium solid solutions

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5YO_{1.5}-10CeO₂-85ZrO₂ solid solution doped with vanadium was studied by means of electron paramagnetic resonance (EPR). The nature of the vanadium species formed by treatment of samples with O₂, CO, and H₂ was investigated. Three types of paramagnetic V⁴⁺ ions found in samples evacuated at 723 K have been attributed to tetragonally compressed octahedral complexes of vanadyl type with different interionic V–O distances. Two of them are supposed to be located on the surface of the oxide support, whereas the third type is in the bulk of the solid. EPR spectroscopy of all CO reduced samples showed the presence of isolated mononuclear V⁴⁺ species. Reducing treatment of the samples with H₂ also provoked the formation of aggregated V⁴⁺ species. The later species formed either by the agglomeration of surface isolated V⁴⁺ ions during high-temperature treatment or the reduction of polymerized V⁵⁺ species present in as-prepared samples. Obtained results can be used for the better understanding of vanadium effect on catalysts properties.

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1. Introduction

Recently, much effort is devoted to the elaboration of catalysts for the treatment of automotive exhausts, which must, simultaneously, oxidize CO and hydrocarbons and reduce NO.

The conventional three-way catalysts (TWCs) containing precious metals are capable to catalyze effectively the mentioned reactions, but only in the case when the contents of oxidants and reductants in gas mixture are near the stoichiometric relationship. The deviation from this value limits essentially their application in automobile converters, since the composition of exhaust gas flow oscillates in a wide range [1–5].

The sensitivity of the TWCs to the oscillations of gas composition can be diminished by the addition of CeO₂, which acts like an oxygen buffer by releasing/storing O₂ due to capability of this oxide to change easily its oxidation state depending on a composition of gas atmosphere [5]. It is known that oxygen exchange properties and thermal stability of CeO₂-ZrO₂ solid solutions are much better than those of CeO₂ [5–8], and the addition of yttrium improves strongly their mechanical proper-

ties [9, 10], which are very important for automotive catalysts.

The mentioned properties of the ternary oxides compatible with high activity of supported vanadium oxides in many red-ox reactions (the oxidation of SO₂ [11], CO [12] and hydrocarbons [13]; the selective catalytic reduction of NO with NH₃ [14] etc.) allow to consider V-containing Y₂O₃-CeO₂-ZrO₂ systems as perspective candidates for replacing the traditional TWCs.

Indeed, it has been found [15] that V-loaded xYO_{1.5}-10CeO₂-(90-x)ZrO₂ solid solutions (x = 5, 10 mol%) were very effective in the NO + CO reaction (which is a key stage in the catalytic control of automotive exhausts), and the catalysts reduced with H₂ exhibited much better activity than treated with CO or oxidized samples. Obviously, not only the composition of the support, but also the oxidation state of the vanadium plays an important role in the reactivity of the catalyst.

In the present work the oxidation state of the vanadium species and their environment formed by treatment of V-containing 5YO_{1.5}-10CeO₂-85ZrO₂ samples with O₂, CO, and H₂ are studied by means of

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electron paramagnetic resonance (EPR). This technique gives information concerning the structure of surface vanadium-oxygen complexes as well as of the nature of vanadium paramagnetic centers incorporated into diamagnetic solids.

2. Experimental

2.1. Preparation of samples

We have prepared the support of the following composition (in mol%) $5\text{YO}_{1.5}\text{-}10\text{CeO}_2\text{-}85\text{ZrO}_2$ (denoted as Y-5).

The support was synthesized by co-precipitation of hydroxides of yttrium, cerium and zirconium by adding ammonium hydroxide to a solution containing the mixture of nitrates of appropriate metals (pH = 10.5–11) with the desired Y/Ce/Zr ratio. The synthesized sample was dried at a temperature range from 373 to 393 K for 5 h and calcined in air at 823 K for 5 h.

Vanadium-containing Y-5 samples were obtained by the impregnation of the support with ammonium metavanadate solution and were dried in air at $373 \div 393$ K for 5 h and calcined in air at 723 K for 3 h. They are denoted as $n\text{V}/\text{Y-5}$, where n is the concentration of vanadium (n was 0.5, 1 and 3 wt%).

All samples were subjected to various treatments before registration of EPR-spectra. Conditions of the treatments were following:

- 1) heating of a sample at 723 K (2 h) followed by evacuation at 723 K for 2 h;
- 2) oxidation of vacuum-treated sample with dry O_2 (40 Torr, 723 K, 0.5 h) with subsequent cooling and outgassing at 293 K (oxidizing treatment);
- 3) reduction of vacuum-treated sample with H_2 (40 Torr, 723 K, 0.5 h) and outgassing at 723 K (reducing treatment);
- 4) reduction of 723 K evacuated samples with CO at room temperature at 50 or 60 Torr for 0.5 h (named as treatment with CO).

2.2. EPR measurements and computer simulation of V^{4+} EPR spectra

EPR measurements were carried out at 77 and 293 K on an EMX Bruker spectrometer (X-band). The concentration of paramagnetic species in the samples was estimated by comparison with absolute standard.

The spectral parameters of V^{4+} were determined by fitting the experimental spectra to those simulated on the computer.

The spectra of V^{4+} ions were calculated under assumption that they are described by spin Hamiltonian of an axial symmetry with electron spin $S = 1/2$ and nuclear spin $I = 7/2$:

$$H = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y).$$

The symbols are standard.

The model spectra were computed in the form of the first derivative of EPR absorption spectrum

[16, 17]:

$$S'(H) = \sum_{m_1=-7/2}^{m_1=7/2} \int_0^{\pi/2} W(\vartheta) F'_{m_1}(\vartheta, H) \sin \vartheta d\vartheta,$$

where $W(\vartheta)$ is the orientation-dependent transition probability [18]; $F'_{m_1}(\vartheta, H)$ are first derivatives of individual adsorption lines. We have employed the Gaussian shape of individual resonance. Simulation was made for angle ϑ with step 1° .

In the second order of perturbation theory, the resonance condition for g - and hyperfine tensors is:

$$\begin{aligned} H(\vartheta, m_1) &= \frac{h\nu}{g\beta} - \frac{K m_1}{g\beta} - \frac{A_{\perp}^2 (A_{\parallel}^2 + K^2)}{4g\beta(g_0\beta H_0 - K m_1)K^2} \\ &\times [I(I+1) - m_1^2] - \frac{(A_{\parallel}^2 - A_{\perp}^2)^2}{2g\beta(g_0\beta H_0 - K m_1)K^2} \\ &\times \left(\frac{g_{\parallel} g_{\perp}}{g^2} \right)^2 \times \sin^2 \vartheta \times \cos^2 \vartheta \times m_1, \end{aligned}$$

where

$$g^2 = g_{\parallel}^2 \cos^2 \vartheta + g_{\perp}^2 \sin^2 \vartheta$$

and

$$K^2 = \frac{A_{\parallel}^2 g_{\parallel}^2 \cos^2 \vartheta + A_{\perp}^2 g_{\perp}^2 \sin^2 \vartheta}{g^2}.$$

The best-fit parameters were determined by a variation of the parameters of spin Hamiltonian (A_{\parallel} , A_{\perp} , g_{\parallel} , g_{\perp}), their standard deviations from average values ($\sigma_{A_{\parallel}}$, $\sigma_{A_{\perp}}$, $\sigma_{g_{\parallel}}$, $\sigma_{g_{\perp}}$), and the coefficients of correlation (τ_{\parallel} , τ_{\perp}) inside $\{A_{\parallel}, g_{\parallel}\}$ and $\{A_{\perp}, g_{\perp}\}$ pairs, respectively.

3. Results

Vanadium-oxygen complexes can simultaneously exist in different structural and oxidation states, which are strongly dependent on the processing conditions (temperature, oxidizing or reducing atmosphere, etc). Obviously, the knowledge of the nature of vanadium species, created by various treatments of samples, can give useful information for understanding vanadium-containing behavior systems in certain catalytic processes.

According to the conditions of preparation of vanadium-containing samples (calcination in air at 723 K), vanadium in as-prepared samples was expected to be in the fully oxidized (V^{5+}) or in the partially oxidized ($\text{V}^{5+} + \text{V}^{4+}$) states. In order to determine their oxidation states, before EPR measurements all samples were subjected to oxidizing treatment under conditions similar to those of synthesis (see Section 2.1).

We found no EPR signals corresponding to V^{4+} ions in the spectra of the samples treated with O_2 . This allows to assume that vanadium in as-prepared samples was in the fully oxidized V^{5+} state, which is EPR silent.

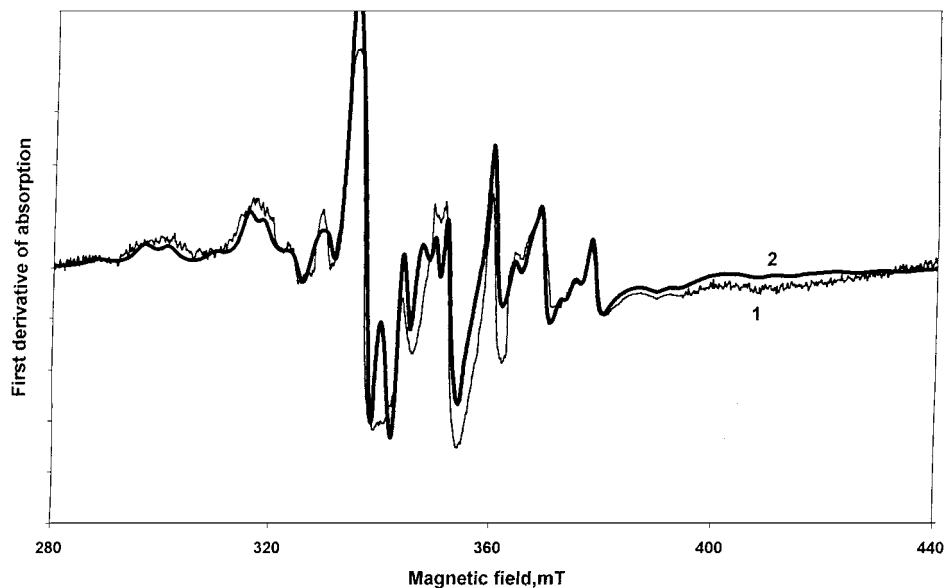


Figure 1a EPR spectra of vacuum-treated 3V/Y-5 sample: (1) experimental, (2) calculated (Fig. 1b).

3.1. Vacuum treated samples

The treatment of samples in vacuum at 723 K led to the appearance of EPR signals, which can be unambiguously attributed to V^{4+} ions. We eliminate the possibility of assignment of these signals to V^{3+} ($S = 1$; $I = 7/2$) or V^{2+} ($S = 3/2$; $I = 7/2$) paramagnetic ions. Indeed, the d^2 (V^{3+}) ions are not stable, moreover the detection of EPR signals from these ions in octahedral fields is difficult because of the very short spin-lattice relaxation time. EPR spectra from V^{3+} in corundum (O_h with slight trigonal distortion) are observed only at 1.3 or 4.2 K [19–21]. However, all the spectra studied in the present work were observed even at room temperature. In tetrahedral fields, EPR signals from V^{3+} (ZnTe, CdTe, ZnZnS, CdS, ZnO) are easily observed but the patterns of the lines [20, 22–24] are quite different from the lines observed in this work. In case of

V^{2+} ions, the perpendicular components of EPR signal should be observed in low fields (less than 200 mT) [22, 24, 25], but all studied experimental spectra were situated in the 270–440 mT range.

Fig. 1a shows the experimental and calculated spectra for 3V/Y-5 vacuum-treated sample. The fragment of computed spectrum from 280 to 400 mT is shown in Fig.1b. The calculated spectrum was obtained as a superposition of four EPR signals. Three of them were calculated for V^{4+} ions using formulae given in Section 2.2. The best-fit parameters of spin Hamiltonian for these three signals (A'' , B'' and C) are given in Table I.

The concentration of V^{4+} centers (as amount of spins, N_x) was determined by double integration of EPR spectrum of V^{4+} signal and comparison with the reference spectrum ($N_{ref} = 2 \times 10^{16}$ spins). The

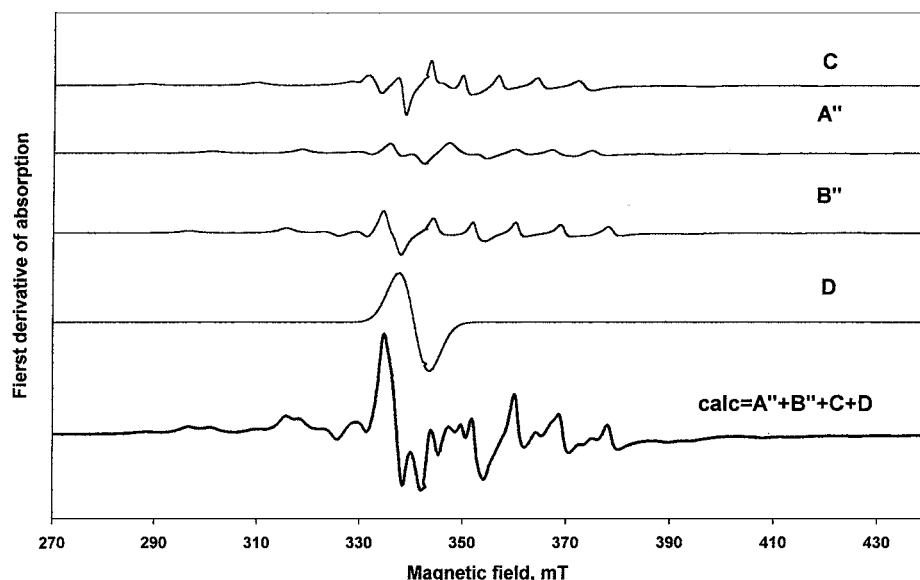


Figure 1b Calculated EPR signals, which were used for the construction of total simulated spectrum, and total calculated spectrum for vacuum-treated 3V/Y-5 sample.

TABLE I Parameters of spin Hamiltonian of V^{4+} in vanadium-containing Y-5 samples

No.	Treatment	Centre	g_{\parallel}	g_{\perp}	$A_{\parallel}, 10^{-4} \text{ cm}^{-1}$	$A_{\perp}, 10^{-4} \text{ cm}^{-1}$
1	Reduced in CO	A'	1.913 ± 0.003	1.979 ± 0.005	180 ± 2	70 ± 4
2	Reduced in CO	B'	1.926 ± 0.003	1.971 ± 0.005	158 ± 2	57 ± 4
3	Vacuum treated	A''	1.910 ± 0.003	1.979 ± 0.005	184 ± 2	70 ± 4
4	Vacuum treated	B''	1.920 ± 0.003	1.971 ± 0.005	160 ± 2	57 ± 4
5	Vacuum treated	C	1.914 ± 0.003	1.983 ± 0.005	192 ± 2	60 ± 5

V^{4+}/V_{total} ratio was found as $(N_x/N_{\text{theor}}) \times 100\%$ ($N_{\text{theor}} = m \times N_A / \text{Mr}$, where m -mass of vanadium in a sample, $N_A = 6,02 \times 10^{23}$, Mr-molecular mass of vanadium). The ratio V^{4+}/V_{total} was ~ 15 , 10 and 3% for 0.5 V/Y-5, 1 V/Y-5 and 3 V/Y-5, respectively. The rest of vanadium was in V^{5+} state. The fourth signal (D) was almost an isotropic line with $\Delta H_{\text{pp}} \sim 5.8$ mT and $g = 2.045 \pm 0.005$.

3.2. Reduced samples

The reduction of the vacuum-treated samples with CO at room temperature results in some increase of concentration of isolated V^{4+} in comparison with that of evacuated samples. The EPR spectra of 0.5V/Y-5 and 1 V/Y-5 samples treated with CO is the superposition of two signals (A' and B'). The components of the C-type spectrum appear only for 3% of vanadium sample.

Fig. 2a shows EPR experimental and calculated spectra of 0.5V/Y-5 sample reduced in CO. The calculated spectrum was obtained as a superposition of the A' and B' signals shown in Fig. 2b (from 280 to 400 mT). The parameters of spin Hamiltonian of these spectra are given in Table. It should be noted that spectral parameters of vacuum-treated and reduced samples differs slightly, and they can be noted as A-, B- and C-spectra. The weak distinctions between, for example, A' and A'' spectra can be due to slightly various local environments of paramagnetic ions.

The treatment of samples with H_2 at 723 K leads to essential increase in the intensity of EPR spectra re-

lated to paramagnetic V^{4+} species. Computer simulation shows that EPR signals of isolated V^{4+} complexes of A-, B- and C-type are superimposed on a broad ($\Delta H_{\text{pp}} \sim 60$ mT) structureless isotropic ($g_{\text{iso}} \sim 1.96$) line. Simulated and experimental spectra of the 3V/Y-5 reduced with H_2 sample are shown in Fig. 3. The calculated spectrum (c) was obtained as a superposition of experimental EPR spectrum of vacuum-treated 3V/Y-5 sample (a) and the broad isotropic signal with $g_{\text{iso}} \sim 1.96$ (b). The simulated spectra of 0.5V/Y-5 and 1V/Y-5 reduced by H_2 samples were obtained by the same way.

4. Discussion

According to literature data (for example [26–28]), local environment of V^{4+} ions in solids can be formed by compressed or elongated octahedra as well as by tetrahedron. In the case of tetrahedral coordination (for example, in zircon or zircon-structured crystals [28]) EPR spectra of V^{4+} were observed at 4.2 K or 77 K because of short spin-lattice relaxation time. Since the EPR spectra of V^{4+} ions in the studied solids are observed at room temperature we can eliminate the possibility of tetrahedral coordination of V^{4+} ions in these materials.

Information concerning the local environment of V^{4+} can be also extracted from EPR spectral parameters. For example, for crystals with rutile structure [27], where V^{4+} is in an elongated octahedron of D_{2h} symmetry, the ground state of V^{4+} ion is a mixture

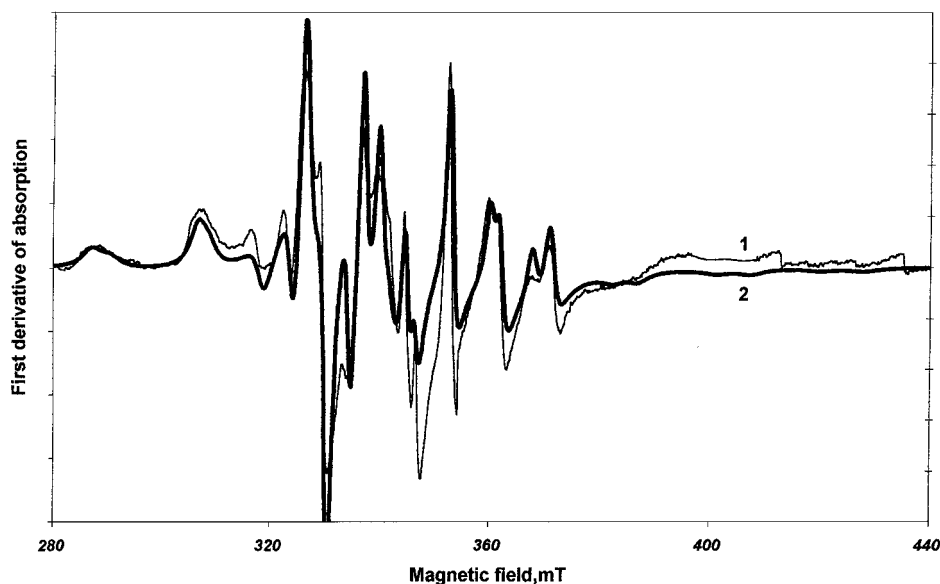


Figure 2a EPR spectra of treated with CO 0.5V/Y-5 sample: (1) experimental, (2) calculated (Fig. 2b).

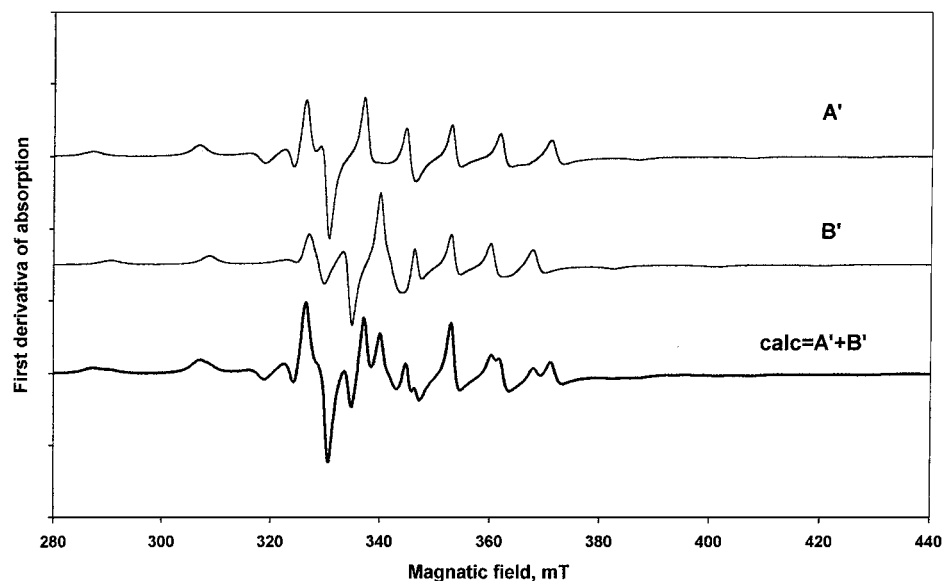


Figure 2b Calculated EPR signals, which were used for the construction of total simulated spectrum, and total calculated spectrum for sample 0.5V/Y-5 treated with CO.

of $|x^2 - y^2\rangle$ and $|z^2\rangle$ functions leading to $g_z > g_x, g_y$ with $A_z > A_x, A_y$ whereas for V^{4+} in compressed octahedron of C_{4v} symmetry with the ground $|xy\rangle$ state $g_{\parallel} < g_{\perp}$ at $A_{\parallel} > A_{\perp}$. The most typical compressed octahedron occurs in the vanadyl complex VO^{2+} with one short $V=O$ bond (distance $R \sim 0.16$ nm), which

is generally coordinated with other groups. For example, the complex $[VO(H_2O)_5]^{2+}$ ion having six-fold coordination occurs frequently and has tetragonal symmetry C_{4v} , in which coplanar bonds are formed between vanadium ion and each of four planar ligands ($r_{V-O} = 0.23$ nm). The vanadyl oxygen is attached axially above the equatorial plane ($r_{V-O} = 0.167$ nm) and the most distant sixth ligand lies opposite to the vanadyl oxygen ($r_{V-O} = 0.24$ nm). In this case the EPR spectra exhibit axially symmetric g - and HFS-tensors [26]. Distortion from pure C_{4v} symmetry is expected to cause the deviation from axial symmetry of A - and g -tensors but the conservation of VO^{2+} as a distinct group requires that the difference between spin Hamiltonian parameters parallel and perpendicular to $V=O$ bond remains large in comparison to the difference between two perpendicular values [26].

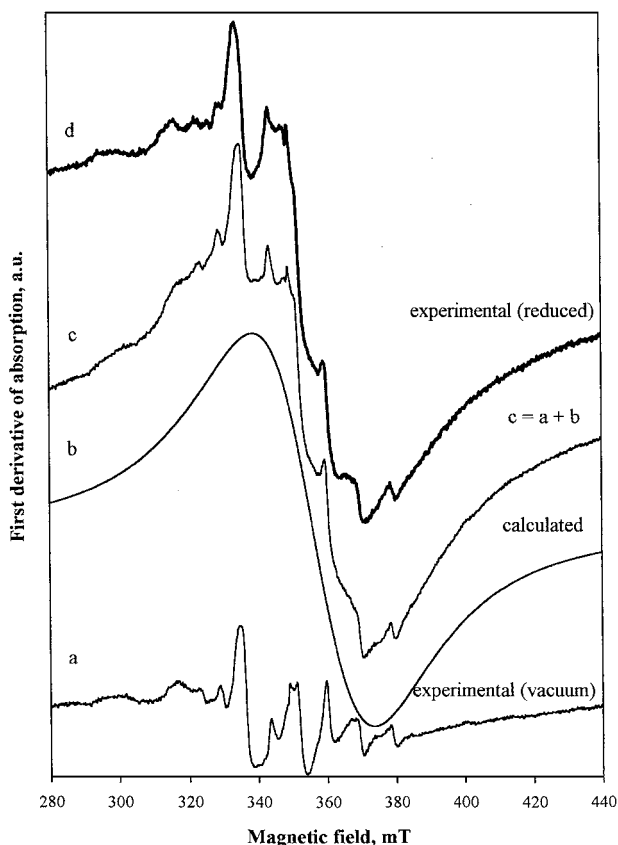


Figure 3 EPR spectra of 3V/Y-5 sample: (a) experimental spectrum of vacuum-treated 3V/Y-5 sample, (b) calculated isotropic signal with $g_{iso} \sim 1.96$, (c) calculated spectrum of reduced in H_2 3V/Y-5 sample obtained as superposition of (a) and (b) spectra, (d) experimental spectrum of reduced in H_2 3V/Y-5 sample.

The relationship between the parameters of spin Hamiltonian given in Table I for three types of V^{4+} species observed in vanadium Y-5 samples indicates that V^{4+} ions are positioned in compressed octahedra with point symmetry close to C_{4v} in all three cases. It is difficult to find theoretical relationship between structure of vanadium complexes and parameters of spin Hamiltonian. Therefore, we made an attempt to state some empiric dependences.

In Fig. 4 the fields of $A_{\parallel}(A_z)$ and $g_{\parallel}(g_z)$ values are presented for some oxide crystals including ZrO_2 -based crystals, oxide glasses and other amorphous and ceramic oxide materials taken from literature.

As follows, from Fig. 4, the spin Hamiltonian parameters of V^{4+} in hydrated crystals (Tutton salts, alums, etc. [26, 29]) shown by the open squares are in a rather narrow range indicating the formation of aqua complexes of vanadyl since the distances between divalent cations (M^{2+}) replaced by VO^{2+} ions and H_2O molecules are sufficient for the adaptation of such complexes. For example, in Tutton salts these distances vary from 0.20 to 0.23 nm [29]. The increase in $V-O$ distances in the equatorial plane of such complexes is

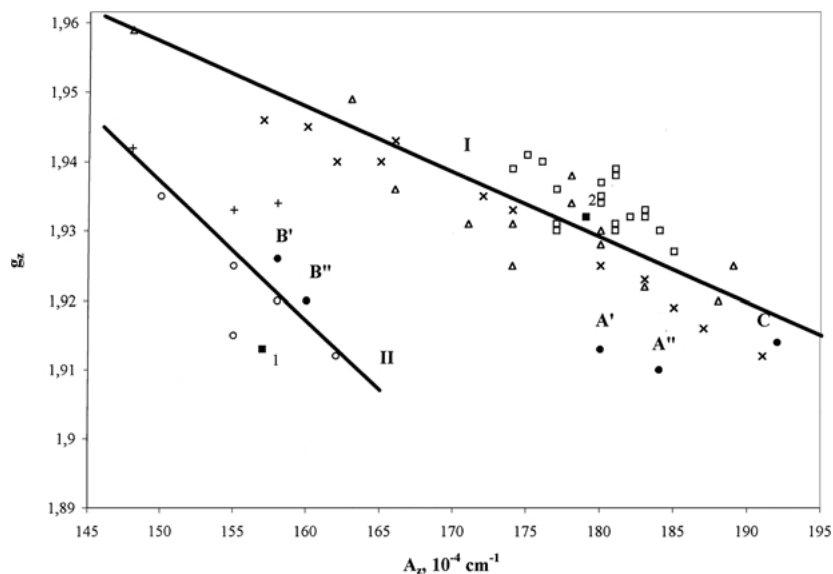


Figure 4 The g_z - and A_z -values of V^{4+} ions in tetragonally compressed octahedron for some oxide crystals, amorphous compounds, ceramics and glasses: \square —hydrated crystals (Tutton salts, alums [26, 29, 30]); Δ —non-hydrated crystals (sulfates, selenates [26], phosphates [41, 42]); \times —oxide glasses [43]; \circ —vanadate glasses [44–46]; \blacksquare —amorphous V_2O_5 [47]; 1— a - V_2O_5 , 2—hydrated V_2O_5 ; $+$ —zirconolite [17]; \bullet —present work.

generally accompanied by an increase in A_z and a decrease in g_z . For example, the increase of bond length V–O from 0.202 to 0.214 nm leads to the increase in A_z (in 10^{-4} cm^{-1}) from 177 to 183 [30].

When VO^{2+} is coordinated only by oxygen atoms (for example, in non-hydrated crystals or oxide glasses), the range of its parameters becomes larger. However, for the majority of these compounds the correlation between changes in A_z and g_z remains. The calculation [231] showed that in oxide glasses g_z decreases from 1.946 to 1.928 and A_z increases from 167 to 178 (in 10^{-4} cm^{-1}) when the V–O distance increases from 0.212 to 0.229 nm. The data for all these materials are situated around straightline I in Fig. 4 (group I).

At the same time, there are oxide compounds for which g -values are similar to those typical of group I ($g_z \sim 1.91$ – 1.945) whereas HFS constants are essentially smaller ($\sim (145$ – $165) \times 10^{-4} \text{ cm}^{-1}$) than those of group I at such g_z -values. The parameters of spin Hamiltonian of these compounds are grouped around straightline II in Fig. 4. Such a behaviour can be due to the considerable distortions of oxygen octahedra and changes of interatomic distances V–O for these compounds in comparison with those of Ist group. For example, in orthorhombic V_2O_5 distances between vanadium and oxygen are $r_1 = 0.158$; $r_2 = 0.178$; $r_3 = r_4 = 0.188$; $r_5 = 0.202$ and $r_6 = 0.278$ (in nm) [32]. It is shown [32] that $A_z = 168 \times 10^{-4} \text{ cm}^{-1}$ at $g_z = 1.923$ is observed for this crystal whereas for vanadyl-type complexes, to such a g_z -value, corresponds to $A_z \sim 185 \times 10^{-4} \text{ cm}^{-1}$ (Fig. 4 (I)). Neutron diffraction investigation of vanadate glasses [33], which can be involved in IInd group of compounds (see Fig. 4), showed that the average value $r_{V-O} \sim 0.18$ – 0.19 nm. As follows, from Fig. 4, spectral parameters of V^{4+} in the zirconolite ceramics belong to the same group II. As shown, V^{4+} ions replace titanium in the lattice of zirconolite [17] for which the mean interatomic Ti–O distances vary from 0.193 to 0.2006 nm [34].

Therefore, we assume that the g_z -value ranging between 1.915 and 1.945 together with $A_z = (145$ – $165) \times 10^{-4} \text{ cm}^{-1}$ belongs to V^{4+} ions in the compressed oxygen octahedron with interionic distances in equatorial plane $r_{V-O} \leq 0.2$ nm.

Thus, as follows from Fig. 4, all tetragonally compressed octahedral complexes of V^{4+} ions can be divided into two groups depending on the relationship between $A_{II}(A_z)$ and $g_{II}(g_z)$. We assume that the difference between complexes entering each of two groups is related to the V–O interionic distances.

As seen in Fig. 4, the spectra of A- and C-types observed in the present work are in the Ist group of complexes whereas the spectra of B-type belong to the IInd group. We assume that the species responsible for A- and C-spectra are located on the surface of oxide support and the species responsible for B-spectra are in the bulk. Indeed, the parameters of spin Hamiltonian of spectra B-type coincide within experimental errors with those for V^{4+} in cubic single crystals $(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$ equal to $g_{II} = 1.933 \pm 0.005$; $g_{\perp} = 1.972 \pm 0.005$; $A_{II} = (155 \pm 3) \times 10^{-4} \text{ cm}^{-1}$ and $A_{\perp} = (50 \pm 5) \times 10^{-4} \text{ cm}^{-1}$ [35]. According to this work V^{4+} occupies cation site of crystalline lattice or is located in the center of empty oxygen cube. Short V–O bond is directed along [110] axis of crystal. In addition, by means of temperature-programmed reduction method, certain of vanadium ions are located in the bulk of solid solution [15].

As follows, from Fig. 3, in the spectrum of the sample treated with H_2 at 723 K the broad isotropic line at $g_{ef} = 1.96$ is present. Both the absence of a hyperfine structure and the large line-width of the isotropic line arise from dipolar or/and exchange interactions among paramagnetic species. It allows to assign this signal to aggregated V^{4+} ions. Similar lines have been observed for many compounds with high concentration of V^{4+} ions [36, 37].

Double computer integration of both total simulated spectra and the broad isotropic line allowed to estimate the concentrations of isolated (A, B, and C) and aggregated V^{4+} species in H_2 reduced samples. It was found that the amount of isolated V^{4+} species decreased and that of aggregated V^{4+} species increased with increasing vanadium loading. So, the ratio of concentrations of isolated V^{4+} ions to aggregated ones was $\sim 4\%$ for 3V/Y-5 sample. It is possible, that the formation of aggregated V^{4+} species can be resulted not only from the aggregation of surface isolated V^{4+} ions during high-temperature treatment, but also from the reduction of polymerized V^{5+} species being present in freshly prepared samples [38].

As seen in Fig. 1b in the spectrum of the samples treated in vacuum a single isotropic line with $g = 2.045$ and $\Delta H_{pp} \sim 5.8$ mT was observed. It should be noted that the identification of the rather narrow line with g near g_e (where g_e is g -factor of free electron) is difficult. The most probable candidate for appearance of D -line can be one of molecular ions of oxygen. On the basis of the g -value, we attribute this line to O^- ions coupled by exchange interaction. EPR spectrum of O^- is characterized by strongly anisotropic g -values (for example, $g_1 = 1.95$; $g_2 = g_3 = 2.234$ for $CaCO_3:NO_3$ or $g_1 = 2.0017$; $g_2 = g_3 = 2.072$ [39]). However, in the limit of the strong exchange interaction the spectrum is characterized by effective g -factor $g_{ef} = 1/3 (g_{II} + g_2 + g_3)$ where g_1, g_2, g_3 are principal components of g -tensor [40]. For O^- ion g_{ef} varies from 2.01 to 2.1 in different compounds [39]. g -Factor of D -line lies in this range. Therefore, we assume that the O^- ion is the most probable candidate for the appearance of D -line. This is formed presumably in the interior of the support due to highly defective structure of crystalline lattice. For other oxygen ions (O^{2-}, O^{3-}, O^{2+}) $g_{ef} < 2.01$ [39].

5. Conclusion

It was shown that in oxidized samples after evacuation the vanadium was in the fully oxidized (V^{5+}) state. Evacuation of samples at 723 K led to the appearance of isolated V^{4+} species of A-, B- and C-type, which were attributed to tetragonally compressed octahedral complexes of V^{4+} with different interionic V—O distances. The analysis of literature data indicates that the spectrum of B-type belongs to V^{4+} ions located in the bulk of solid solution. After evacuation of samples their treatment with CO an increase of isolated V^{4+} species concentration was mentioned (by comparison with amount of isolated species stabilized on and in support during vacuum pretreatment).

Reducing treatment of the samples with H_2 provoked the formation of aggregated V^{4+} species. It was found that both total concentration of paramagnetic V^{4+} species and concentration of aggregated V^{4+} ones increased whereas concentration of isolated species decreased with increasing vanadium content.

The knowledge of the nature of the vanadium species in the oxidized and reduced with CO or H_2 V-loaded 5YO_{1.5}-10CeO₂-85ZrO₂ samples, exhibiting rather dif-

ferent activity in the NO + CO catalytic reaction (see Introduction), is very important for understanding the mechanism of this catalytic process. Determination of active sites responsible for the conversions of NO and CO over the V-containing 5YO_{1.5}-10CeO₂-85ZrO₂ catalysts is in progress and these data will be reported in a following paper.

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