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The Electron Spin Resonance of Oxovanadium Sulfate Dispersed on Porous Materials

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Oxovanadium sulfate was fixed on silica and alumina gel bases as a model of the oxidation catalyst. On silica gel the ESR spectra showed an exchange narrowing without hyperfine lines as a result of the formation of small crystallites. In this case, axially-symmetrical g factors were obtained: $g_{\perp}=1.969\pm0.001$ and $g_{\parallel}=1.915\pm0.005$. When sulfuric salts of alkali metals were added to the system, the dispersion of VO^{2+} ions became homogeneous and a hyperfine structure was observed in the ESR spectra. On an alumina gel base the spectrum resembled that of the frozen aqueous solution of $VOSO_4$ and showed the hyperfine structure, $A_{\perp}=(7.0\pm0.2)\times10^{-3}\text{cm}^{-1}$ and $A_{\parallel}=(1.85\pm0.05)\times10^{-2}\text{ cm}^{-1}$. It may be considered that VO^{2+} ions are distributed homogeneously in the surfase layer of alumina. In the alumina gel and silica gel with alkali sulfate, the decrease in the V^{4+} ions with heat treatment was slower than in the silica gel system.

Vanadium complexes which are fixed on various base materials have been used for oxidation catalysts. The mechanism of their catalytic reaction and the effects of added materials have been investigated by many authors from the point of view of kinetics or of structure.[1-10]

Recently some investigators[11-14] have analyzed the electronic structure of V^{4+} or VO^{2+} in the catalyst system. The V^{4+} ion has a single unpaired electron in the 3d orbital and shows the ESR spectrum with eight hyperfine lines as a result of V^{51} ($I=7/2$). Fortunately, the studies about V^{4+} and VO^{2+} have been stored up from the theoretical point of view in the relation of the ESR spectra from various states.[15-24]

In this paper, the circumstances of the VO^{2+} ions in a catalytic system with silica or alumina gel bases will be investigated by the ESR method. The interaction between oxovanadium sulfate and base materials will be discussed, as well as the effects of the addition of the sulfates of alkali metals.

Experimental

Sample Preparation. — Oxovanadium sulfate, $VOSO_4 \cdot 3H_2O$, was prepared by the reduction of vanadium(V) oxide with sulfur dioxide. Silica and alumina gels were immersed in an aqueous solution at varying concentrations of oxovanadium sulfate and sulfuric acid. They were then dried and kept in an air bath at 120°C for 10 hr. Five kinds of alkali sulfate, lithium sulfate, sodium sulfate, potassium sulfate, cesium sulfate and ammonium sulfate, were added to aqueous solutions of $VOSO_4$.

TABLE I. SAMPLES

Base material	$VOSO_4$ content	Alkali sulfates added to the system
Silica gel Alumina gel	5—40% of base materials	Li_2SO_4; Na_2SO_4; K_2SO_4; Cs_2SO_4; $(NH_4)_2SO_4$

ESR Measurements. — The ESR spectra were measured at two frequencies, the X and K bands. The K-band spectrometer was a super-heterodyne type constructed by the Oyo Denki (Applied Electric) Laboratory Co., Ltd., while the X-band spectrometer was made in the authors' laboratory. The magnetic field was monitored with the proton resonance at an accurately known frequency. As a standard of the signal intensity, a small ruby crystal and calcium oxide powder containing Mn^{2+} were employed.

Results and Discussion

The ESR of VO^{2+} in Aqueous Solutions.— The ESR signals of the VO^{2+} ions in aqueous solutions were measured as a function of the concentrations of VO^{2+} and sulfuric acid in order to examine the ionic configuration of VO^{2+}. In the concentration range from 0.1 to 3 mol./l. of VO^{2+}, a typical hyperfine structure of eight lines was observed. The width of the hyperfine components changed with the nuclear spin quantum number, m_I. At a more concentrated solution of VO^{2+}, it became impossible to observe the separate hyperfine structure. When sulfuric acid was added to the solutions where the hyperfine components were distinguished, however, the individual hyperfine width became broad, probably because of an increase in the viscosity. The addition of alkali metal ions did not affect the spectra.

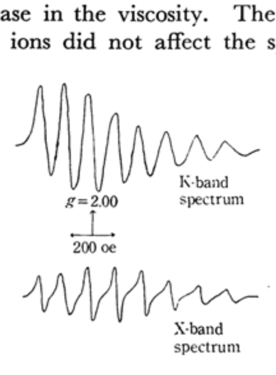

Fig. 1. ESR spectrum of $VOSO_4$ in aqueous solution (0.1 mol./l.).

Kivelson,[15] Rogers and Pake[16] have given the following equation for the width of the hyperfine components of VO^{2+} in solutions:

$$\Delta H = a_0 + a_1 m_I + a_2 m_I^2 \qquad (1)$$

where ΔH is the width, m_I is the nuclear spin quantum number, and a_0, a_1, a_2 are as follows:

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$$a_0=\alpha+\tau_c[4/45(\varDelta\gamma H_0)^2+3/40I(I+1)b^2] \qquad (2a)$$

$$a_1=\tau_c[4/15(b\varDelta\gamma H_0)] \qquad (2b)$$

$$a_2=\tau_c[1/8b^2] \qquad (2c)$$

where α is the contribution from unspecified sources, τ_c is correlation time, $H_0=\omega_0/\gamma$, $\varDelta\gamma=\beta(g_\perp-g_\parallel)$, and $3b=2(A_\parallel-A_\perp)$. In Eqs. 2a, 2b and 2c the small terms are neglected.

The values of α and the $\varDelta\gamma H_0/b$ ratio have been calculated; they are listed in Table III. The values of α are not in good agreement, as the line shapes of the hyperfine components are not symmetric and the theory is not sufficient to describe the broadening mechanism. The $\varDelta\gamma H_0/b$ ratio should be 2.5 times larger in the K-band spectra than in the X-band spectra. Actually, however, the results obtained are from 1.9 to 2.8 times larger in the former.

TABLE II. VARIATION IN THE WIDTHS OF HYPERFINE LINES IN THE ESR SPECTRA OF VO^{2+} IN AQUEOUS SOLUTIONS

Concentration		Width parameters[1]			
VO^{2+} mol./l.	H_2SO_4 N	a_0 œ.	a_1 œ.	a_2 œ.	
3.0	0	63.5	4.7	1.2	k)
		19.7	2.3	1.7	x)
1.0	0	57.6	10.5	2.2	k)
		13.1	1.4	0.6	x)
0.1	0	29.5	7.2	1.4	k)
		6.6	0.6	0.2	x)
0.1	0.1	26.2	6.3	1.3	k)
0.1	1.0	25.9	6.0	1.3	k)
		7.9	1.0	0.4	x)
0.1	3.0	26.0	6.0	1.3	k)
		8.7	0.7	0.3	x)
0.1	10	35.0	8.0	1.5	k)

1) The meanings of a_0, a_1 and a_2 are given in Eq. 1.
k) K-band measurement.
x) X-band measurement.

It may be considered from these data that the electronic structure around VO^{2+} does not change greatly in the solution at from 0.1 to 1.0 mol./l. VO^{2+} concentration nor upon the addition of up to 3 N of sulfuric acid. A distorted octahedral structure of $VO(OH_2)_5$, which has been proposed for dilute aqueous solutions of VO^{2+} ions, can be considered.[24] When the concentration of VO^{2+} ions or that of sulfuric acid increases, not only the change in viscosity but also the change in the structure of coordination around VO^{2+} must occur.

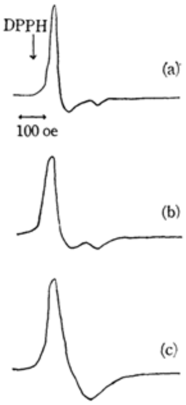

Fig. 2. (a) ESR spectrum of powdered $VOSO_4\cdot3H_2O$. (b) ESR spectrum of $VOSO_4$ on silica gel base; $VOSO_4$ content: 10 mol.%. (c) ESR spectrum of $VOSO_4$ on silica gel with Na_2SO_4; Na_2SO_4: 10 mol.%.

VO^{2+} Ions on Silica Gel Base.—Oxovanadium sulfate dispersed on silica gel shows an ESR spectrum of an axial symmetrical g anisotropy without a hyperfine structure (Fig. 2), which resembles the ESR spectra of $VOSO_4\cdot3H_2O$ and of $VOSO_4\cdot H_2SO_4$ in powder. In these systems, the exchange narrowing becomes dominant and the hyperfine interaction is negligible as compared with the g

TABLE III. ESR CONSTANTS OF VO^{2+} IN AQUEOUS SOLUTIONS

Concentration		g Factor	Hyperfine constant	α	$\varDelta\gamma H_0/b$	
VO^{2+}, mol./l.	H_2SO_4, N	$<g>$	$<A>\times10^2$, cm^{-1}	œ.		
3.0	0	1.962		52	1.8	k)
			1.16	3.4	0.64	x)
1.0	0	1.962	1.20	45	2.2	k)
			1.17	7.0	1.1	x)
0.1	0	1.962	1.22	15	2.4	k)
			1.19	4.3	1.2	x)
0.1	0.1	1.960	1.22	13	2.3	k)
0.1	1.0	1.962	1.21	13	2.2	k)
			1.19	4.2	1.2	x)
0.1	3.0	1.966		13	2.2	k)
			1.2	5.8	1.2	x)
0.1	10	1.962	1.2	19	2.4	k)

k) K-band measurement. x) X-band measurement.

anisotropy for the K-band measurements. The VO^{2+} ions seem to form small crystallites of $VOSO_4 \cdot nH_2O$. Therefore, if each individual csystallite is distributed in random orientation and gives Lorentzian line shape, the ESR spectrum may be expressed approximately as follows:[25]

$$I(H)=\int K\sin\theta \cdot \frac{d\theta}{(H-H_0)^2+b^2} \qquad (3)$$

where H_0 is the resonance field, θ is the angle between the applied field H and the crystal axis, $K=1/8\,g_\perp{}^2[(g_\parallel/g_\perp)^2+1]$, and b is the half-width at the half-power of each crystallite.

The values of $g_\perp$, $g_\parallel$ and b can be estimated from the experimental data, if b remains constant throughout the θ range. The results are listed in Table IV.

TABLE IV. ESR CONSTANTS OF $VOSO_4$ ON SILICA GEL BASE

Additional material	g Factor			Width ΔH_{msl}
	$g_\perp$	$g_\parallel$	$<g>$	
none	1.969	1.915		36
			1.963*	64*
10%LiSO	1.965	1.90		55
	1.968*	1.91*		50*
10%Na_2SO_4			1.967	46
10%K_2SO_4			1.956	60—70
10%Cs_2SO_4			1.955	80—90
10%$(NH_4)_2SO_4$	1.970	1.912		31
$VOSO_4 \cdot 3H_2O$**	1.976	1.913		26
	1.974*	1.90*		28*
$VOSO_4 \cdot H_2SO_4$**	1.976	1.90		20

The quantity of $VOSO_4$: 10 mol.% of base material.

The quantity of alkali sulfate: 10 mol.% of base material.

* Measured after heat treatment at 300°C.

** Without base material.

When the sample was heated in a stream of air, the ESR signal decreased in intensity, while the width was increased. As the symmetry of the spectrum increased, only an apparent value of g could be obtained. The exchange narrowing, therefore, seems to become weak as a result of the decrease in the concentration of VO^{2+} ions, while the ill-resolved hyperfine structure seems to cause the inhomogeneous broadening.

When alkali sulfates were added to the system, the hyperfine structure appeared in the ESR spectrum. This effect was influenced by the quantity of alkali sulfate as well as by its kind. In Fig. 4 the change in the hyperfine splitting of the system with various concentrations of cesium sulfate is shown. When the mole ratio of cesium sulfate to the silica gel base reached about 0.4, the width of each individual hyperfine component was about 40 oe. and the splitting between the components had the value noted.

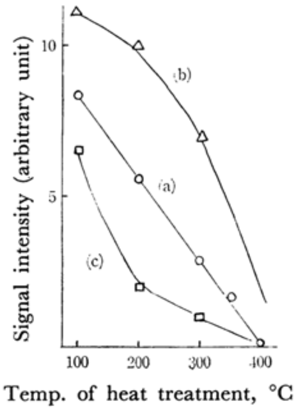

Fig. 3. The Variation of the ESR intensity of $VOSO_4$ on silica gel with heat treatment; (a) without additional material, (b) with Na_2SO_4, (c) with $(NH_4)_2SO_4$. The content of $VOSO_4$ and of additional materials are 10 mol.% to base.

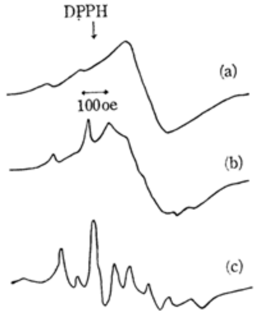

Fig. 4. The variation of ESR spectra of $VOSO_4$ on silica gel as a function of the additional quantity of Cs_2SO_4; 1) 10 mol.%, 2) 20 mol.%, and 3) 40 mol.%. $VOSO_4$ content is about 10 mol.%.

The samples containing alkali sulfate gave complicated spectra as a result of the anisotropy of g as well as that of the hyperfine structure. From the figure of the narrowing spectrum, it may be assumed that the axial symmetry exists for both g and hyperfine tensors, with $g_\perp > g_\parallel$ and with $A_\perp < A_\parallel$. Some hyperfine components which appear in the low magnetic field have highly-distorted signal shapes in the K-band measurements. On the other hand, in the X-band measurements, it is easy to obtain the value of $A_\parallel$, but difficult to determine $g_\perp$, $g_\parallel$ and $A_\perp$.

If both g and hyperfine tensors have an axial symmetry and if each ion is distributed at rondom, the ESR spectrum may be expressed as follows:[26]

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$$I(H)=\frac{1}{(2I+1)}\sum_{m_I=-7/2}^{7/2}\int_0^1 K(\theta)\cdot S(H-H_0)^2\cdot \mathrm{d}z \tag{4}$$

where $z=\cos\theta$, θ and $K(\theta)$ have meanings given in Eq. 3, $S(x)$ is the shape function, and $S(H-H_0)=1/\{(H-H_0)^2+b^2\}$ for Lorentzian. Including the magnetic hyperfine interaction to the second order, the resonance field is given approximately by:

$$\begin{aligned}H_0 = H_c &- Km_I/g\beta - (4H_c)^{-1}(g\beta)^{-2}A_\perp{}^2\\ &\times (A_\parallel{}^2+K^2)K^{-2}[I(I+1)-m_I{}^2]\\ &-(2H_c)^{-1}(g\beta)^{-2}(A_\parallel{}^2-A_\perp{}^2)^2\\ &\times K^{-2}g_\perp{}^2g_\parallel{}^2g^{-4}z^2(1-z^2)m_I{}^2\end{aligned} \tag{5}$$

where $H_c=h\nu/g\beta$, $g^2=g_\perp{}^2+(g_\parallel{}^2-g_\perp{}^2)z^2$ and

$$K^2g^2=A_\parallel{}^2g_\parallel{}^2z^2+A_\perp{}^2g_\perp{}^2(1-z^2)$$

$A_\perp$ and $A_\parallel$ are hyperfine-structure constants in energy units.

By comparing the K-band spectra to the above expressions, we can obtain $g_\perp$, $A_\perp$, and $A_\parallel$, because the K-band spectra shows the characteristic signal from those crystallites which have orientations perpendicular to the magnetic field. When $z=0$, Eq. 5 becomes:

$$\begin{aligned}H_0(m_I) = H_\perp &- A_\perp m_I/g_\perp\beta - (4H_\perp)^{-1}(g_\perp\beta)^{-2}\\ &\times (A_\perp{}^2+A_\parallel{}^2)(63/4-m_I{}^2)\end{aligned}$$

where $H_\perp=h\nu/g_\perp\beta$. The results are listed in Table V.

When the quantity of alkali sulfate remains only ten percent of the base materials, the values of $g_\perp$ and $g_\parallel$ can not be determined separately, but they give an apparent value of $g:\langle g\rangle=(2g_\perp+g_\parallel)/3$. When the hyperfine splitting is so large that Eq. 5 is applicable, the values of g obtained are slightly greater than those of the sample without alkali sulfate, The values of $A_\perp$ appear to be $6.3\times10^{-3}\,\mathrm{cm}^{-1}$ for the sample with 20% cesium sulfate, and $7.5\times10^{-3}\,\mathrm{cm}^{-1}$ for that with 40% cesium sulfate.

The decrease in the ESR intensity with heat treatment is slower for the systems containing alkali sulfates than for the system without them, except for the case of ammonium salt. Alkali sulfates make the ESR of VO^{2+} insensitive to the heat treatment. They prevent the oxidation of vanadium ions from 4+ to 5+ and the formation of crystallites of vanadium(V) oxide,

VO^{2+} on an Alumina Gel Base.—Oxovanadium sulfate on an alumina gel base showed ESR spectra closely resembling those of the system of a silica base with alkali sulfate in the concentration range from 5 to 10 percent of $VOSO_4$. The addition of alkali sulfates did not have any remarkable effects. Table V shows the results obtained by the method described in the preceding section. As the concentration of $VOSO_4$ increased, the width of each hyperfine component exceed the hyperfine splitting. The ESR spectrum was observed as a broad single line which had a good symmetry.

TABLE V. ESR CONSTANTS OF $VOSO_4$ IN ALUMINA GEL AND IN SILICA WITH ALKALI SULFATES

Sample		g	Hyperfine constant	
Base	Additional material		$A_\parallel\times10^2$ cm^{-1}	$A_\perp\times10^3$ cm^{-1}
Silica	20% Cs_2SO_4			6.26
Silica	40% Cs_2SO_4	1.978	2.2	7.52
Silica	40% $(NH_4)_2SO_4$	1.980	2.0	7.52
Alumina	none	1.967	1.92	6.41
Alumina	10% Li_2SO_4	1.968	1.86	6.58
Alumina	10% Na_2SO_4	1.968	1.86	5.95
Alumina	10% $(NH_4)_2SO_4$	1.964	1.92	5.95
		1.965*		6.85*

$VOSO_4$ content: 10 mol.% of bsse material
* Measured after heat treatment at 300°C.

VO^{2+} Ions in an Aqueous Solution at 77°K.—The ESR spectra of $VOSO_4$ in aqueous solution at 77°K are shown in Fig. 5. In aqueous solutions containing under 0.1 N sulfulic acid, the hyperfine lines show a broadening in spite of the low concentration of $VOSO_4$. In the solutions containing over 1.0 N sulfuric acid, on the contrary, the sharp hyperfine components were clearly separated. This system can be considered to be a typical model of the random distribution of VO^{2+} ions. The values of $g_\perp$, $A_\perp$, $A_\parallel$ can be calculated by using Eq. 5; they are listed in Table VI. They are in good agreement with the results obtained from the data on an alumina gel base.

From the variation in spectra with the different concentrations of sulfuric acid, the existence of

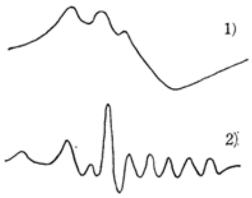

Fig. 5. ESR spectra of $VOSO_4$ in aqueous solutions observed at 77°K. 1) VO^{2+}: 0.1 mol./l., 2) VO^{2+}: 0.1 mol./l., H_2SO_4: 1 N.

TABLE VI. ESR CONSTANTS OF $VOSO_4$ IN AQUEOUS SOLUTIONS AT 77°K

Concentration		g	Hyperfine constant	
VO^{2+} ion mol./l.	H_2SO_4 N		$A_\parallel\times10^2$ cm^{-1}	$A_\perp\times10^3$ cm^{-1}
0.1	0.3			7.28
0.1	1.0		2.9	7.37
0.1	3.0	1.965	2.3	7.05
0.1	10.0	1.966	2.3	7.16

excess SO_4^{2-} ions may be considered to change the circumstances around VO^{2+} ion, or the coordination state of VO^{2+}.

The Effects of Base Materials and Alkali Sulfates.—Silica gel has a weaker interaction with transition metal oxides dispersed on it than has alumina gel.[27] Oxovanadium sulfate is deposited as small crystallites on silica gel, and so the ESR of VO^{2+} on silica shows the exchange narrowing.

When alkali sulfates are added to the system, double salts, $M_2 \cdot V_2O_2(SO_4)_3$, are formed[28] and the exchange between VO^{2+} ions is prevented. An excess addition of alkali sulfates bring about a dilution of the double salt and a decrease in the width of the hyperfine lines in the ESR spectrum. If the random dispersion of VO^{2+} ions is realized at an adequate concentration, an ESR with a hyperfine structure can be observed. Frozen sulfuric acid solutions of VO^{2+} are good models for this state. The spectra obtained with an alumina base are similar to those of the frozen sulfuric acid solutions. VO^{2+} ions may be considered to be combined strongly with an alumina base and to be dispersed homogeneously in the surface layers of almuina.

Summary

The electron spin resonance spectra of oxovanadium sulfate has shown an exchange narrowing on a silica gel base as a result of the formation of small crystallites. In this case, the g factor has an axial symmetry of $g_\perp = 1.969 \pm 0.001$ and $g_\parallel = 1.915 \pm 0.005$. When alkali sulfates are added to the system, the dispersion of VO^{2+} ions on the base materials becomes homogeneous and ESR spectra with hyperfine lines appear.

On an alumina gel base, VO^{2+} ions seems to be dispersed homogeneously in the surface layers of the base, and ESR spectra show the hyperfine structure with the parameter of $A_\perp = (7.0 \pm 0.2) \times 10^{-3}\ \mathrm{cm}^{-1}$ and $A_\parallel = (1.85 \pm 0.05) \times 10^{-2}\ \mathrm{cm}^{-1}$. These values are slightly smaller than the value of $\langle A \rangle$, $(1.20 \pm 0.03) \times 10^{-2}\ \mathrm{cm}^{-1}$ which has been obtained from aqueous solutions of VO^{2+}.

The authors are indebted to Messieurs Nobuhisa Goto, Kunihiko Nakamura and Hiroshi Fukunaga for their kind help in the ESR measurements and for their discussions.

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