WETNESS EFFECT ON EPR Cu(II) SPIN LABEL IN HEAT TREATED SILICA XEROGELS

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Received 27. 2. 1995

The present paper deals with drying of SiO_2 xerogel that leads to the decrease of the intensity of Cu(II) spin probe EPR signal and to the signal/noise ratio as well. This effect is explained by changes of Cu(II) coordination into an EPR less sensitive one. During a sample dehydration the decrease of electric permittivity causes the increase of the dipole dipole interaction between Cu(II) coordination polyhedra, which plays an important role in decreasing EPR signal.

INTRODUCTION

The sol-gel process is a new method which is applied to the preparation of glasses or catalysts. It involves the transformation of a homogeneous solution or sol, formed by an alcoholic solution of alkoxides, water and appropriate additives into a gel. Using the special thermal treatment the resulting gel may be further converted to glass. Sol-gel processing of inorganic glasses offers many advantages over the traditional melt processing techniques such as greater homogeneity and purity, lower processing temperatures, and better control over the glass properties. Using this process the molecular structure of the product can be controlled by changing the reaction conditions and/or the gel thermal treatment. Electron paramagnetic resonance (EPR) is often applied for structural study of sol-gel oxide glasses.

Transition metal ions are widely used as EPR spin labels in structural study of heat treated xerogels prepared by sol-gel method [1-15]. The structural evolution of SiO_2 xerogel during its calcination using Cu(II) spin label was investigated by Darab and MacCrone [3,7]. In our study of an ageing of heat treated (at various firing temperatures) SiO_2 xerogels with introduced Cu(II) spin label the problems connected with EPR spectra reproduction have appeared [16]. The analysis of this phenomenon indicated that an ambient humidity could effect the line shape and the intensity of the obtained Cu(II) EPR spectra. The experimental verification of this hypothesis is the main contribution of the presented work.

EXPERIMENTAL PART AND RESULTS

The SiO_2 xerogels were prepared according to Darab and MacCrone method [3,7]. The solution of the composition: 39.19 mol% ethyl alcohol, 11.47 mol% i-propyl alcohol, 9.79 mol% tetraethyl orthosilicate, 39.27 mol% distilled water and 0.29 mol% HCl was used. The Cu(II) spin label was introduced during the hydrolysis as $CuCl_2.2\ H_2O$ (at the concentration cca 10^{-3} mol dm^{-3}). The dry gel was crushed to powder and heated at 280 °C for six hours. The temperature was increased up to 360 °C and the samples were heated for three hours. Then the xerogel samples were taken out of the furnace and cooled to the room temperature in the presence of the desiccator. The temperature 360 °C from the interval of the xerogel firing temperatures (280 - 800 °C) was chosen, because at this temperature was observed the simplification of multicomponent Cu(II) EPR spectra to one component spectra, so called "Γ_1" spectrum [3,7]. The prepared xerogel samples were exposed to the environment with well defined partial pressure of water vapour (2.7 kPa) at five different temperatures ranging from 18 to 96 °C until reaching equilibrium. The details of this experimental equipment are described elsewhere [17]. The water contents related to the dry weight at various exposure temperatures are given in Table I.

Cu (II) EPR spectra were measured on a BRUKER 200 E - SRC X-band EPR spectrometer at room and liquid nitrogen temperatures. 100-kHz modulation was used. For illustration, the Cu(II) EPR spectra of SiO_2 xerogel samples with various water contents measured at 77K are shown in Figure 1.

Table I. The water contents related to the dry weight of the SiO_2 xerogel equilibrated at different exposure temperatures at partial H_2O pressure of 2.7 kPa.

Sample number	Relative mass uptake (%)	Temperature (°C)
1*	0.75	room temperature
2	-1.35	96
3	0.35	75
4	4.78	54
5	11.26	26
6	15.18	18

* Control sample-stored under air at room temperature

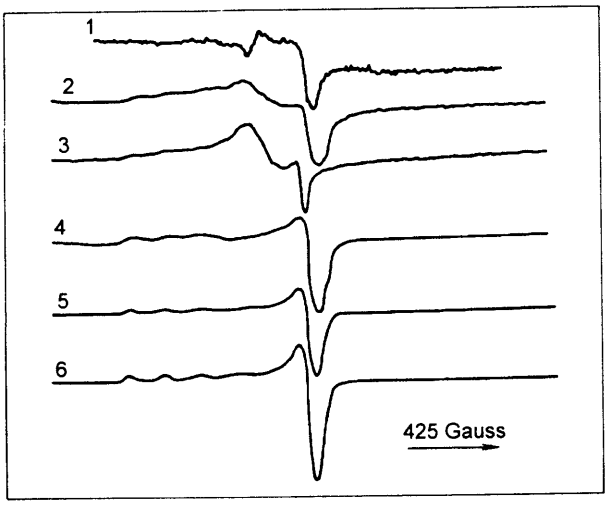

Figure 1. Cu(II) EPR spectra of SiO_2 xerogels calcinated at 360 °C , for different contents of water measured at 77 K. For numbering see Table I

The spin Hamiltonian of Cu(II) ion in axially symmetric crystal field prevalent in xerogel samples is given by the equation [12,18]:

$$\hat{H} = \beta B \overline{\overline{g}} \hat{S} + \hat{S} \overline{\overline{A}} \hat{I} \qquad (1)$$

where B is the vector of the external magnetic field induction, $\hat{S}$ is the vector operator of the electron spin momentum, $\hat{I}$ is the vector operator of the nuclear spin momentum, g is the g-factor tensor, β is the Bohr magneton, $\overline{\overline{A}}$ is the hyperfine interaction tensor. (For axial symmetry the principal components of g-tensor and A-tensor are reduced on the perpendicular and parallel ones to z axis: $g_\perp = g_{xx} = g_{yy}$, $g_\parallel = g_{zz}$, $A_\perp = A_{xx} = A_{yy}$, $A_\parallel = A_{zz}$; respectively).

Expanding the terms for the diagonalised tensors the axial symmetric spin Hamiltonian is given:

$$\hat{H} = \beta g_\parallel B_z S_z + \beta g_\perp (B_x S_x + B_y S_y) + A_\parallel I_z S_z + A_\perp (I_x S_x + I_y S_y) \qquad (2)$$

The resonance condition for axial symmetric spectra takes a form:

$$B_M^\circ = \frac{h\lambda + MA_{ef} + [(h\lambda + MA_{ef})^2 - \lambda_M]^{1/2}}{2\beta g_{ef}} \qquad (3)$$

where:

$$g_{ef} = (g_\perp^2 \sin^2 \vartheta + g_\parallel^2 \cos^2 \vartheta)^{1/2}$$

$$A_{ef} = \frac{(A_\perp^2 g_\perp^2 \sin^2 \vartheta + A_\parallel^2 g_\parallel^2 \cos^2 \vartheta)^{1/2}}{g_{ef}}$$

$$\lambda_M = \frac{1}{4A_{ef}^2} [I(I+1) - M^2][A_\parallel^2 A_\perp^2 + A_{ef}^2 A_\perp^2] + \frac{M^2}{2A_{ef}^2} [A_\perp^2 - A_\parallel^2] \left[\frac{g_\perp g_\parallel}{g_{ef}^2}\right]^2 \sin^2 \vartheta \cos^2 \vartheta$$

where is B_M° - a resonance field for M projection of the spin nuclear number of Cu nucleus, h - Planck constant, β - Bohr magneton, ν - klystron frequency, I - spin nuclear number of Cu nucleus (I=3/2), ϑ - an angle between the main axis of g - tensor and the external magnetic field vector.

The dependence of the obtained spectra on the external magnetic field induction B can be expressed by the Lorentz derivation bands:

$$Y(B) = N \int_0^{\pi/2} \sum_M P(\vartheta) \frac{B - B_M^\circ}{\Delta B} \left\{1 + \frac{4[B - B_M^\circ]^2}{3\Delta B^2}\right\}^{-2} \sin \vartheta \, d\vartheta \qquad (4)$$

where N is normalisation constant.

Transition probability $P(\vartheta)$ is given by the following equation [18]:

$$P(\vartheta) = g_\perp^2 [g_\perp^2 \sin^2 \vartheta + g_\parallel (1 + \cos_2 \vartheta)] \qquad (5)$$

The fact, that the half-width of spectral line is a complicated function of particle orientation is caused by both the complex structure of xerogel and long relaxation time [12]:

$$\Delta B = \{\Delta B_\perp^2 \sin^2 \vartheta + \Delta B_\parallel^2 \cos^2 \vartheta\}^{1/2} \qquad (6)$$

where $\Delta B_{\perp}$ and $\Delta B_{\parallel}$ are perpendicular and parallel components of half-width, respectively.

The general details of interpretation and analysis of Cu(II) EPR spectra in SiO_2 xerogels measured at room and liquid nitrogen temperatures were given previously [3, 7, 10, 12].

The spin Hamiltonian parameters and the half-width of the spectral lines were obtained by non-linear regression analysis of 77K EPR spectra. The line shape function and the more details about the non-linear regression analysis of transition metal ions EPR spectra in the SiO_2 xerogels are described elsewhere [10, 12, 13].

The results of this analysis are shown in Table II. The unambiguous optimal estimates of the spin Hamiltonian parameters $g_{\perp}$, $g_{\parallel}$, $A_{\parallel}$, and line half-width ($\Delta B_{\perp}$, $\Delta B_{\parallel}$) were obtained only for the xerogel samples with sufficient contents of moisture. Only this results are presented in Table II.

Table II. The obtained estimates of spin Hamiltonian parameters and line-width parameters for Cu(II) in SiO_2 xerogels measured at 77K, and for different contents of the water. The statistically significant results were obtained only in the case of sufficiently wet samples. (The standard deviations are indicated in brackets)

Sample number	$g_{\perp}$	$g_{\parallel}$	$\Delta B_{\perp}$ (10^{-4} T)	$\Delta B_{\parallel}$ (10^{-4} T)	$A_{\parallel}$ (10^{-4} T)
4	2.0659 (0.0002)	2.4431 (0.0086)	41.596 (0.59)	29.123 (1.90)	76.682 (3.90)
5	2.0707 (0.0002)	2.4630 (0.0093)	36.218 (0.40)	16.519 (2.15)	79.971 (3.90)
6	2.0701 (0.0002)	2.4638 (0.0074)	35.889 (0.41)	18.822 (1.85)	79.184 (3.50)

DISCUSSION

It is obvious from presented results, that drying of SiO_2 xerogels decreases the intensity of Cu(II) EPR signal and affects the signal/noise ratio. So that, it is impossible to analyze measured spectra.

The similar effect was observed by Tominaga et al. [1] during a thermal desorption of ammonia molecules from silica gel using $[Cu(NH_3)_4](NO_3)_2$ spin label. It may be explained by changes of Cu(II) coordination into EPR less sensitive one. This suggestion was supported by the fact, that after the re-exposition of the treated samples to ammonia the line shapes and intensities of EPR spectra were almost the same as the original ones [1].

The decrease of electric permitivity during a sample dehydration can also cause the increase of the dipole-dipole interactions between Cu(II) coordination polyhedra. These interactions play an important role in decreasing of EPR signal intensity, as well. Such kind of interactions was considered in the work of Ikoma et al.[5].

The effect of the increasing intensity and the improvement of the signal/noise ratio by wetting of xerogel samples can not be (at the given experimental arrangement) caused by the changes of oxidation state of the Cu(II) ion. This fact is supported by the reversibility of the drying - hydration process, too.

We suggest, that observed phenomenon can be explained by the simultaneous effect of the above mentioned mechanisms.

CONCLUSION

The presented results show, that it is important to take into account the effect of wetness on the xerogel samples with implanted Cu(II) spin label during EPR structural investigation. The more detailed analysis will be the object of our future work.

Acknowledgement

This work was supported under grant No 999437/93 by Slovak Grant Agency for Science.

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Submitted in English by the authors

VPLYV VLHKOSTI NA EPR SPEKTRÁ SPINOVEJ SONDY Cu(II) V TEPELNE SPRACOVANÝCH XEROGÉLOCH OXIDU KREMIČITÉHO

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Počas dehydratácie xerogélov oxidu kremičitého dochádza k znižovaniu pomeru signál/šum v EPR spektre spinovej sondy Cu(II). Tento efekt sa sledoval na sérii vzoriek xerogélov ktoré boli uvedené do rovnováhy s konštantnou tenziou vodnej pari pri rôznych teplotách. Zvlhčenie sa určilo relatívnou zmenou hmotnosti vzoriek (Tab I.). Len v dostatočne zvlhčených vzorkách bolo možné regresnou analýzou určiť parametre spinového hamiltoniánu.Uvedený efekt sa vysvetluje zmenou koordinačného polyédra Cu(II), ku ktorej dochádza v dôsledku deficitu kyslíkov z molekúl vody a súčasne vzrastom dipól-dipólových interakcií spôsobeným znížením dielektrickej permitivity pri dehydratácii vzoriek.