Vanadium Ions in Sol–Gel Silica Studied by Electron Spin Resonance, UV-Visible Absorption, Diffuse Reflectance, and Photoluminescence Spectroscopies

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ESR, 紫外–可視吸収, 拡散反射, ホトルミネッセンス分光法による ゾル–ゲルシリカ中のバナジウムイオンの研究

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Valence states and structures of vanadium species supported on silica, which were synthesized by a sol-gel method, were studied by Electron Spin Resonance (ESR), UV-visible absorption, diffuse reflectance, and photoluminescence spectroscopies for various stages of the process (sols, xerogels and heated xerogels). ESR measurements revealed that V^{4+} ions were present as $[VO(H_2O)_5]^{2+}$ in sols and xerogels for a lower vanadium concentration, whereas a higher vanadium concentration led to the aggregation of V^{4+} ions in the drying stage of the sol-gel process. Upon calcinations at a higher temperature of 873 K, the V^{4+} ions were oxidized to V^{5+} which, for a lower vanadium concentration, were located in isolated pseudotetrahedral silica sites, and with an increase in the vanadium content, were aggregated so that V_2O_5 was finally formed. Changes of pseudotetrahedral structure to octahedral one by the coordination of water molecules in the atmosphere were observed, especially when the xerogels was heated at a lower temperature of 973 K.

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1. Introduction

Supported vanadium oxide is an intriguing material because of its catalytic and photocatalytic applications.^(1–5) A clue for understanding their properties can be attained through a knowledge of the structures of vanadia. Therefore there have been many studies on them by using various spectroscopic methods.^(6–15) Among them, the photoluminescence of pentavalent vanadium (V^{5+}) ions supported on silica is of quite interest.^(1,3,16–18) The photoluminescence at 77 K had the vibrational progression of 1050 cm^{-1} and the lifetime of about 20 ms, for which it was assigned to the phosphorescence from the lowest triplet state of the pseudotetrahedral oxovanadium chromophore.⁽¹⁶⁾ The pseudotetrahedral oxovanadium has three basal-plane oxygens and a terminal double bonded oxygen. The lowest triplet state was generally attributed to the ligand-to-metal charge transfer (CT) state associated with the $V=O$ bond.^(1,3,16) A recent study, on the contrary, argued that the lowest excited triplet state possibly involved promotion of an electron from the basal plane ligands (O) to the metal center (V^{5+}) and not from the terminal $V=O$ bond.⁽¹⁸⁾ The nature of the triplet state is still an open question.

The synthesis of the silica-supported vanadium oxide is employed by using a sol-gel process,^(12,14,15,18–21) which makes it possible to study the formation mechanisms and structures of vanadium species at molecular scale by the sol-gel process. In our previous reports, we characterized with Electron Spin Resonance (ESR) technique tetravalent vanadium (V^{4+}) ion-doped silica through sol-to-gel transformation,⁽¹⁹⁾ and studied optical properties of the pseudotetrahedral oxovanadium chromophores supported on silica after heat treatment of the dried gels.⁽²⁰⁾ In this paper, we shall report in detail valence states and structures of the vanadium species in silica from sols to heated gels via a drying process, by means of several spectroscopic techniques.

niques.

2. Experimental

The following reagents were used without additional purification: $VOSO_4 \cdot 2H_2O$ (Kojundo Chem. Labo.), tetramethoxysilane (TMOS; Tokyo Kasei Kogyo), methanol (Katayama Chem. Ind.), and HCl (Wako Pure Chem. Ind.). Water was deionized and distilled. An aqueous solution of $VOSO_4 \cdot 2H_2O$ (7.2 ml) and 2.0 ml of 1 M HCl were mixed, to which TMOS dissolved in methanol (15 ml/15 ml) was added. The molar ratio of TMOS: water was 1:5. In the following the nominal amount of vanadium (V) ions in silica gel is expressed as 100 times of the molar ratio of V/Si. The mixtures were stirred for 0.5 h and allowed to be gelled at room temperature in polystyrene beakers sealed by a plastic film with several pinholes. The resultant gels were dried in the polystyrene beakers in air at room temperature over 3 months. They were further calcined from 873 to 1273 K for 1–4 h in air.

ESR spectra measurements were performed at 296 K with a JEOL JES-RE1X spectrometer using X band. The microwave power was 30 mW and the modulation amplitude, 0.2 mT. A Mn marker was used to calibrate a magnetic field. Diffuse reflectance UV-visible spectra were taken at room temperature on a JASCO V-570 spectrophotometer. Steady-state luminescence spectra were recorded at 77 K on a JASCO FP-770 spectrofluorometer. Luminescence decay profiles were obtained with a N_2 laser (Usho AN-200) and a photomultiplier (Hamamatsu Photonics R955).

3. Results and discussion

3.1. Valence-states and coordination number of vanadium ions in silica

Figure 1 shows the ESR spectra of V^{4+} -doped sols and xerogels dried over 3 months under the various V:Si molar

Fig. 1. ESR spectra of V^{4+} -doped silica sols just prepared and xerogels dried over 3 months for various V concentrations.

ratios. Eight lines of a hyperfine structure ($A_{av} = 11.2$ mT) assignable to $[VO(H_2O)_5]^{2+}$ were observed in the spectrum of the sol at $100\text{ V/Si} = 0.1$ (a), which arose from the almost complete averaging of g anisotropy owing to the "tumbling motion" of the $[VO(H_2O)_5]^{2+}$.^{19,21} A very similar ESR spectrum was also observed for the dried sample (b), indicating that the tumbling motions in the silica gel pores were as fast as those in sols. As shown in the previous paper,¹⁹ this fast motion ceased when the xerogels were dehydrated in vacuum and started again after the dehydrated xerogels were left in the ambient atmosphere for a day or so. These results showed that V^{4+} ions were not directly bonded with the siloxane network structure but trapped as $[VO(H_2O)_5]^{2+}$ in the silica gel pores. With increasing V

Fig. 2. Absorption spectra of xerogels dried over 3 months at $100\text{ V/Si} = 1$ and 10 .

Fig. 3. Diffuse reflectance UV-visible spectra of samples heated at 1273 K for 4 h for various V concentrations: $100\text{ V/Si} = 0.1$ (a), 1 (b), 5 (c) and 10 (d).

concentration, a broad signal overlapped with the well-defined signal came to be observed for the xerogels; it slightly appeared at $100\text{ V/Si} = 1$ (c) and became predominant at $100\text{ V/Si} = 5$ (d). The broad signal with $g \approx 1.98$ is attributed to aggregations of V^{4+} ions.^{4,21} Moreover, the fact that the broad signal was scarcely observed for the sol (e) and the wet gel (not shown here), even at $100\text{ V/Si} = 10$ but became significant for the xerogel dried over 3 months (f) indicate that the aggregations were formed during the drying stage of gels. Figure 2 shows the absorption spectra for the xerogels at $100\text{ V/Si} = 1$ and 10 . A broad absorption band at 760 nm accompanying with a shoulder around 640 nm were obtained, which is ascribed to oxo-vanadium complexes of $[VO(H_2O)_5]^{2+}$.^{14,15} There seems to be no clear indication of a new band due to aggregations in contrast to the ESR spectra in Fig. 1.

With thermal treatment in air the ESR signals due to V^{4+} decreased and became undetectable above 873 K , corresponding to which the absorption band with a peak at 760 nm due to $[VO(H_2O)_5]^{2+}$ disappeared. Figure 3 shows the

absorption spectra of the samples heated at 1273 K for 4 h with various V concentrations. The spectrum of 100 V/Si = 0.1 (a) exhibited a peak at 242 nm and shoulders at 220 and 290 nm. The spectrum is very close to previous results,^{3),9)} where these bands were generally assigned to the oxygen-to-vanadium charge transfer (CT) transitions in dispersed pseudotetrahedral V⁵⁺. The appearance of the blue-shifted band at 220 nm as well as the main peak at 242 nm suggests the presence of more distorted pseudotetracoordinated V⁵⁺ (band at 220 nm) in addition to the dominant pseudotetra-coordinated V⁵⁺ (band at 242 nm).^{9),22)} With increasing the V concentration, a spectral broadening and shift to longer wavelength were observed at 100 V/Si = 1 (b) and 5 (c). These changes can be ascribed to the aggregations of pseudotetrahedral V⁵⁺, because isolated species generally give rise to CT transitions in a higher energy range than polymeric species as explained by the size effects.⁷⁾ In addition, a broad band at around 400 nm appeared at 100 V/Si = 10 (d). The visible band agrees with that of V₂O₅ in vanadia-silica systems.^{3),7),9),23)} Small microcrystalline domains of V₂O₅ were found at higher concentrations in vanadia-silica prepared by the sol-gel process.^{4),23),24)} Actually the X-ray diffraction pattern of the calcined gel showed weak reflections at $2\theta = 21.5^\circ$ and 26.1° corresponding to the crystalline V₂O₅.²⁴⁾ Considering these results together, the formation of V₂O₅ at 100 V/Si = 10 can be concluded. These spectral changes with an increase in the V concentrations coincide with the broad signal in the ESR spectra thus confirming that the concentrated V⁴⁺ in the dried gels was converted to the aggregations of pseudotetrahedral V⁵⁺ ions (100 V/Si = 5) and V₂O₅ (100 V/Si = 10) after calcinations. In aqueous solutions, a variety of V⁵⁺ species can be formed, depending on the solution pH and vanadium oxide concentration; namely, more polymerized and complex vanadium oxide species such as V₁₀O₂₆(OH)₂⁴⁻ and crystalline V₂O₅ are formed with decreasing the solution pH or increasing the vanadium oxide concentration.²⁵⁾ Therefore, the several species found in this experiment are not unexpected.

3.2 Phosphorescence properties of silica-supported vanadium oxide

Figure 4 shows the phosphorescence spectra of the samples heated at 1273 K for 4 h with various V concentrations. The spectra became blurred gradually and the intensities decreased with an increase in the V content. At 100 V/Si = 10 (e), the spectrum showed the poorly resolved structure and had a shifted peak at 558 nm with the intensity of about one twentieth of that at 100 V/Si = 0.1 (a). These spectra changes coincided with those found in the absorption spectra shown in Fig. 3. Based on the absorption spectra, the red shifted and blurred vibrational structure in the phosphorescence can be ascribed to the formation of aggregated pseudotetrahedral V⁵⁺. The decreased phosphorescence intensity is attributed to decreasing of the isolated pseudotetrahedral V⁵⁺ due to the formation of aggregated pseudotetrahedral V⁵⁺ and V₂O₅, because the phosphorescence was observed for tetrahedral vanadium species dispersed on silica but not for bulk V₂O₅.³⁾

The phosphorescence lifetimes were obtained from the decay curves monitored at the phosphorescence peaks. The lifetimes can be fitted by a sum of two exponential decays (Eq. 1):

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \quad (1)$$

where $A_1 + A_2 = 1$. Table 1 shows the lifetimes of two decays (τ_1 and τ_2) and the relative weights of each component (A_1 and A_2) as well as the phosphorescence peaks. The longer lifetime component (A_1) with approximately 10 ms was dominant for the concentration 100 V/Si $\leq$ 1. The A_1 component gradually decreased with the increased V

Fig. 4. Phosphorescence spectra of samples heated at 1273 K for 4 h at 350-nm excitation for various V concentrations: 100 V/Si = 0.1 (a), 1 (b), 5 (c), 9 (d) and 10 (e).

Table 1. Long (τ_1) and Short (τ_2) Lifetimes with Preexponential Factors A_1 and A_2 (in Parentheses) for Phosphorescence Peaks of Various Vanadium Oxide in SiO₂ Calcined at 1273 K and Observed at 77 K

100V/Si	$\lambda_{\max}/\text{nm}$	τ_1/ms (A_1)	τ_2/ms (A_2)
0.1	524	10.8 (0.76)	2.2 (0.24)
1	525	10.0 (0.68)	2.5 (0.32)
3	527	8.4 (0.64)	1.5 (0.36)
5	528	7.8 (0.56)	1.2 (0.44)
9	555	5.5 (0.45)	0.5 (0.55)
10	558	4.9 (0.54)	0.4 (0.46)

contents and the lifetime was finally 4.9 ms at 100 V/Si = 10. The lifetime of the A_2 component also diminishes from 2 to 0.4 ms. The decrease in the lifetimes corresponded well to the decrease in the phosphorescence intensity, suggesting the concentration quenching owing to the aggregations of pseudotetrahedral oxovanadium chromophores.

In Table 2, the wavelengths (ν) and the vibrational frequencies ($\Delta\nu_{i-1,j}$) are summarized for samples calcined at 1173 and 1273 K for 4 h as examples of comparatively resolved spectra. The average vibrational frequency from the 0-1 to 0-3 bands was $\sim 1040 \text{ cm}^{-1}$, which is quite good agreement with that of the V=O stretching band.^{1),3),16),17)} On the other hand, the vibrational frequency through the 0-4 and 0-6 bands was reduced in comparison with that in lower order of vibrational transitions and the average of all

Table 2. Vibrational Frequencies of the Phosphorescence Spectra at 77 K from Vanadium Oxide in SiO₂ (100 V/Si=0.1) Calcined at (a) 1173 K and (b) 1273 K

λ/nm	ν/cm^{-1}	$\Delta\nu_{0,j}/\text{cm}^{-1}$ ($\Delta\nu_{0,i-1} + \Delta\nu_{i-1,j}$)
(a)		
432 (0-0)	23148	0
453 (0-1)	22075	1073
475 (0-2)	21053	2095 (1073+1022)
500 (0-3)	20000	3148 (2095+1053)
524 (0-4)	19084	4064 (3148+916)
551 (0-5)	18149	4999 (4064+935)
580 (0-6)	17241	5907 (4999+908)
(b)		
434 (0-0)	23041	0
455 (0-1)	21978	1063
476 (0-2)	21008	2033 (1063+970)
501 (0-3)	19960	3081 (2033+1048)
525 (0-4)	19048	3993 (3081+912)
552 (0-5)	18116	4925 (3993+932)
583 (0-6)	17153	5888 (4925+963)

was $\sim 980 \text{ cm}^{-1}$. According to Tran et al.,¹⁸⁾ the averaged frequency corresponded to the vibrational band at 977 cm^{-1} attributed to a basal plane V–O stretching mode. However, it is not necessarily adequate to analyze the spectrum by using the average frequency of all bands, because there may be the anharmonicity of the potential for the higher overtone. Therefore, it seems to be preferable to consider that the phosphorescence spectrum consists of the progression of the V=O stretching.

The calcination temperature influenced the stability of the phosphorescent species. Figure 5(a) shows the phosphorescence spectra of a sample at 100 V/Si=0.1 measured just after heating at 973 K and after exposing to be moist air for 3 h. The spectral form of the phosphorescence did not change essentially after 3 h but the intensity reduced to 20% of the initial one, whereas the excitation spectrum corresponding to the CT bands of V⁵⁺ in the pseudotetrahedral coordination showed a decrease in the relative intensity of the 290-nm band against the 240-nm band with the exposure time as shown in Fig. 5(b). Figure 6 shows the absorption spectra of the corresponding samples shown in Fig. 5 measured just after heating at 973 K and successively exposing to the moist air for 3 h. The spectrum of the dehydrated sample had a peak at 244 nm with a shoulder at 290 nm, which decreased in intensity with accompanying an increased tail above 350 nm after 3 h. These spectral changes were ascribed to the formation of octahedral V⁵⁺ due to the coordination of water molecules.^{7,12)} Therefore, the decrease in the phosphorescence intensity observed in Fig. 5(a) can be attributed to a decrease in the pseudotetrahedral V⁵⁺ species. Longer wavelength phosphorescence can be expected from the octahedral V⁵⁺ species for the hydrated samples if emissive. However, no luminescence was observed when excited at the 450-nm band of the octahedral V⁵⁺ species. This can be explained by an increase in the radiationless transition (energy gap law).²⁶⁾

3.3 Structural change of vanadium species in silica

Based on the ESR, UV-visible absorption, and phosphorescence data, the plausible structures for the V species are summarized in Fig. 7. The hydrated vanadyl species in sols and xerogels are $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ (A) for low vanadium concentration. The very fast tumbling motion of $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ (A) for sols and xerogels observed with ESR

Fig. 5. Phosphorescence (a) and excitation (b) spectra of a sample at 100 V/Si=0.1 measured just after heating at 973 K and after exposing to the atmospheric humidity to 3 h.

Fig. 6. Diffuse reflectance UV-visible spectra of a sample at 100 V/Si=0.1 measured just after heating at 973 K and after exposing to the atmospheric humidity for 3 h.

technique indicate that there is little direct bonding between the vanadyl species and silica surface. After calcination, vanadium is oxidized to V⁵⁺ in dispersed pseudotetrahedral silica site (B) which shows the phosphorescence. Water molecules can coordinate in V⁵⁺ to form the octahedral species (C) in air humidity as seen in the spectral changes in the phosphorescence excitation and absorption spectra. Aggregates of vanadyl species (D) are formed for higher vanadium concentration in the drying stage of the sol-gel

Fig. 7. Schematic structural changes proposed for vanadium species in sol, xerogel and heated gels.

process, resulting in a broad ESR signal. One of the possible structure will be a hydroxo-bridged like. On calcination, the aggregates change to pseudotetrahedral V^{5+} aggregates (E) and V_2O_5 for further high vanadium concentration.

4. Conclusions

The V^{4+} ions were present as $[VO(H_2O)_5]^{2+}$ in the sols and xerogels of silica for lower vanadium concentration. The aggregates of V^{4+} ions were formed for higher vanadium concentration in the drying stage of the sol-gel process. After calcination above 873 K, they were oxidized to V^{5+} in dispersed pseudotetrahedral silica site, which showed the phosphorescence spectra with the vibrational progression associated with the $V=O$ bond. By the coordination of water molecules the pseudotetrahedral structure was changed to the octahedral one and the phosphorescence intensity was reduced. This phenomenon was particularly observed when calcined below 973 K. It was also clarified from the results of the phosphorescence and lifetime measurements that the aggregates of V^{4+} ions change to pseudotetrahedral V^{5+} aggregates and crystalline V_2O_5 after calcinations.

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