JOURNAL OF
Materials
CHEMISTRY

Photoredox behavior of methylviologen doped in silica gel matrices

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Received 8th May 2000, Accepted 30th August 2000
First published as an Advance Article on the web 27th October 2000

Silica gels doped with methylviologen (MV), which is a photoredox and photochromic compound, have been prepared under both acidic and basic conditions. The oxidation process of the reduced species, MV^+, formed by UV irradiation of the gels, was investigated on the basis of UV absorption measurements. The magnitude of the absorption maximum of MV^+ in the gels gradually decreased with time after irradiation, as is observed for MV^+ in solution, indicating that the photoredox behavior of MV in the gel matrix is very similar to that in solution. The lifetime of MV^+ increased with increasing microviscosity around MV after gelation in the gels prepared under acidic conditions. The lifetime of MV^+, however, reached a maximum and then gradually decreased as the gel was aged, suggesting that the oxidation of MV^+ to more stable MV^{2+} readily occurred due to the restriction of the diffusion of MV^+ and oxidized solvents. Moreover, the lifetime of MV^+ in the gels prepared under basic conditions reached a maximum at an earlier stage of gel aging than for the gels prepared under acidic conditions because the microviscosity around the MV molecules at the gelation point under basic conditions was greater than that under acidic conditions.

1 Introduction

In recent years much attention has been focused on organic–inorganic composites as new advanced materials. The sol–gel method is one of the most promising techniques for synthesizing organic–inorganic composites. Inorganic gels with the network structure usually observed in oxide glasses can be prepared at room temperature *via* the sol–gel process, so that functional organic molecules with poor thermal stability can be introduced into rigid inorganic oxide matrices without thermal decomposition.[1–4] Many studies of sol–gel-derived composites doped with photofunctional organic molecules have been reported in a variety of fields, such as optical sensors, dye lasers, and so on.[4–13] Another important application is the use of such sol–gel-derived composites to create solid-state photoelectrochemical cells as energy transfer devices. We have previously prepared a silica gel-based composite doped with ruthenium bipyridine complexes, which are important in assembling such solid-state photoelectrochemical cells[4] and sensors.[6] A series of redox molecules have been known to also play an important role as electron transfer molecules in photoelectrochemical cells. Gel composites doped with redox molecules are thus expected to be promising as energy and electron transfer materials in the photoelectrochemical cells.

Methylviologen (1,1′-dimethyl-4,4′-bipyridylium chloride, abbreviated as MV) is a photoredox and photochromic molecule and is used as a redox indicator.[14,15] MV is present as MV^{2+} in solution and is reduced by electron donors (D) to MV^+ under UV irradiation, as shown in eqn. (1).

$$MV^{2+} + D + h\nu \rightarrow MV^+ + D^+ \tag{1}$$

When UV irradiation is stopped, MV^+ is oxidized by any electron acceptor, in some cases even by the oxidized donor molecules D^+ (*e.g.* solvents such as ethanol and methanol in silica gels), as shown in eqn. (2).

$$MV^+ + D^+ \rightarrow MV^{2+} + D \tag{2}$$

Although MV^{2+} has no absorption in the visible region, MV^+ has an absorption at around 608 nm. MV^{2+} has an ability to act as a strong electron acceptor in solution,[16] and is expected to be used as an important component in various photoelectrochemical cells for the utilization of solar energy. The incorporation of MV in oxide matrices is thus a potential route to new solid photoelectrochemical devices and it is therefore important to clarify the fundamental properties, like photoredox behavior, of MV in such composites.

In the present study, we have prepared the MV-doped silica gels under acidic and basic conditions and investigated the disappearance process (oxidation) of the reduced species, MV^+, formed by UV irradiation on the basis of UV absorption measurements. The photoredox behavior of MV doped in the silica gel matrix prepared under acidic and basic conditions is reported.

2 Experimental

Silica sols containing MV (Tokyo Kasei Co.) were prepared under acidic or basic conditions. Under acidic conditions, precursor sols were prepared from tetraethoxysilane, TEOS (Wako Chemicals Co.), distilled ethanol, EtOH (Wako Chemicals Co.), and hydrochloric acid of pH 1. The molar ratio TEOS : EtOH : water was 1 : 4 : 10. MV was dissolved in EtOH and this was mixed with the TEOS and hydrochloric acid to form a transparent sol. The atomic ratio MV/Si was fixed at 3×10^{-2}. Silica sols under basic conditions were prepared by mixing tetramethoxysilane, TMOS (Tokyo Kasei Co.), distilled methanol, MeOH (Wako Chemicals Co.), and aqueous ammonia of pH 10. A mixture of TMOS, aqueous ammonia, and MV dissolved in MeOH was stirred to form a transparent sol. The molar ratio TMOS : MeOH : water was 1 : 4 : 10 and the atomic ratio MV/Si was fixed at 3×10^{-2}.

The resultant sols prepared under acidic and basic conditions were poured into polystyrene cuvettes. The total volume of each sol was about 3 cm^3. The cuvettes were then sealed with a polystyrene stopper. The cuvettes containing sols prepared under acidic and basic conditions were respectively kept at 35 °C and room temperature (*ca.* 25 °C) until gelation occurred. Both gels were aged at 35 °C in the sealed cuvettes. The wet gels hardly shrank during aging because the cuvettes containing the samples were kept sealed. In order to dry the gels, the stoppers

DOI: 10.1039/b003647l

were removed and the cuvettes covered with aluminium foil, leaving a small hole, and kept at 35 °C to allow slow evaporation of the solvent. The dry gels obtained under both the acidic and the basic conditions were free from cracks and transparent.

The sols and gels were irradiated with UV and visible light for 20 min with a 500 W Xe lamp (Ushio Denki Co.). The infrared light was cut off using a colored glass filter (IRA-25S; Toshiba Glass Co.). The light power was *ca.* 5×10^3 W m^{-2}. The temperature of the atmosphere surrounding the sols and gels was about 40 °C owing to thermal emission with the light irradiation.

The absorption spectra of the sols and wet gels were measured on a UV spectrophotometer (JASCO Co., V-560). The macroscopic viscosities of mixed solutions, such as ethylene glycol and water, were measured at 25 °C using a Toki B8M-HM rotating viscometer in order to ascertain the influence of the viscosity of systems on the disappearance process of the reduced species MV^+.

3 Results

3.1 Preparation of MV-doped silica sols and gels

The MV-doped silica sols prepared under both acidic and basic conditions were homogeneous and transparent. When the silica sols were prepared under basic conditions using TEOS instead of TMOS, the TEOS-derived silica sols became inhomogeneous during preparation at the molar ratio TEOS : EtOH : water 1 : 4 : 10. Thus, under the basic conditions, TMOS was used as a starting material in order to prepare homogeneous sols. The gelation periods of the sols prepared under acidic conditions were 100 h at 35 °C, whereas those under basic conditions were 6 h at room temperature. This difference in gelation time is mainly caused by catalytic effects rather than the reactivities of the metal alkoxides, although TMOS is more reactive than TEOS. MV-doped silica gels prepared under both acidic and basic conditions became transparent dry gels without cracks after slow evaporation of the solvent.

3.2 Photoredox behavior of MV-doped silica sols and gels

Fig. 1 shows the variation of the visible absorption spectra of the MV-doped silica wet gels prepared under acidic conditions after irradiation with UV light for 20 min. The MV-doped silica wet gels are colorless before irradiation, as shown in Fig. 1(a). The direction of the arrow corresponds to the passage of time. Absorption bands are observed at around 608 and 400 nm in each spectrum of the MV-doped silica wet gels after irradiation. These spectra are attributed to MV^+ formed by the photoreduction of MV^{2+} [eqn. (1)]. The magnitude of the absorption maximum at around 608 nm gradually decreases with the passage of time after irradiation, that is, the blue colors gradually fade. This change in absorption indicates that MV^+ formed during irradiation gradually disappears with the passage of time after irradiation.

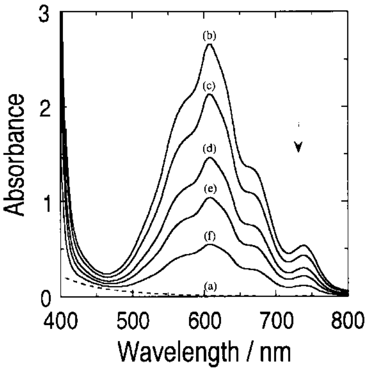

Fig. 1 Variation of the visible absorption spectra of the MV-doped silica wet gels prepared under acidic conditions after irradiation with UV light for 20 min. (a) Gel before irradiation. (b)–(f) Gels 6, 24, 57.5, 84 and 121 min after irradiation, respectively.

Fig. 2 shows the changes in the magnitude of the absorption maximum (608 nm) for the MV-doped silica sols and gels prepared under acidic conditions as a function of time after irradiation. The ordinate in Fig. 2 is plotted as $\ln(A_t - A_0)$, where A_t represents the absorbance at the time t after irradiation and A_0 the absorbance before irradiation. The various storage times at 35 °C of the MV-doped silica sols and gels after mixing the starting materials are indicated on the figure. The gelation time was 100 h and the drying of the gel started about 890 h after storage. All the plots of $\ln(A_t - A_0)$ *vs.* time for each sample are approximately linear, indicating that the oxidation of MV^+ obeys first-order kinetics in the sols and gels. Furthermore, the slopes of the plots gradually become shallower up to a certain point (*ca.* 400 h) in the wet gels (●, ■, ◆, ▼) and then become steeper as the aging process proceeds (○, □, ◇, △, ▽). The changes in the slopes of the plots reflect those in the lifetime of MV^+, therefore the lifetime of MV^+ must change with gel aging.

Fig. 3 shows the lifetime of MV^+ in the silica matrix and the weight loss of the MV-doped silica gels prepared under acidic conditions as a function of storage time. The lifetime is defined as the reciprocal of the slopes of the plots in Fig. 2. The coloration in the aging stage of the wet gels occurred only at the surface which was irradiated owing to the absorption by MV^+ and also scattering of UV light. After the gelation point, the lifetime of MV^+ steeply increases to a maximum at around 400 h storage time and then gradually decreases. The drying was started at the time when the change in the lifetime of MV^+ was hardly observed in the aging process. The lifetime of MV^+ in the gels being dried continues to decrease and the coloration of the gel after irradiation becomes harder to observe. Consequently, it was impossible to calculate the lifetime of the gels in the later stages ($t > 1100$ h) of drying.

Fig. 4 shows the changes in the magnitude of the absorption maximum of MV^+ in the silica matrix after irradiation during the formation process of silica gels prepared under basic

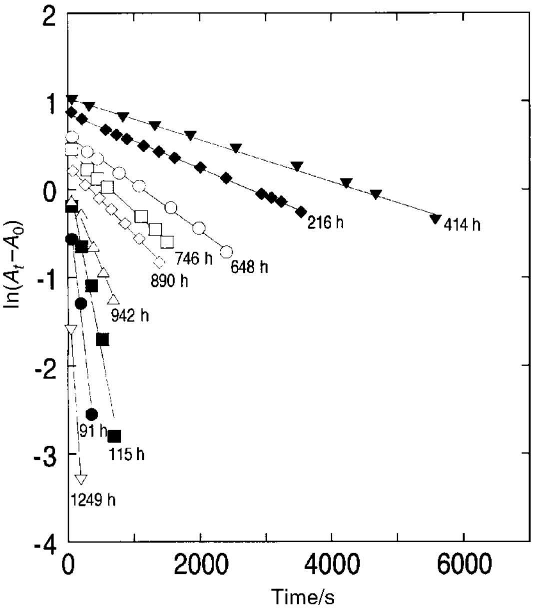

Fig. 2 Changes in the magnitude of the absorption maximum (608 nm) for the MV-doped silica sols and gels prepared under acidic conditions as a function of time after irradiation. The ordinate is plotted as $\ln(A_t - A_0)$, where A_t represents the absorbance at the time t after irradiation and A_0 the absorbance before irradiation. The symbols represent the storage time: ●91; ■115; ◆216; ▼414; ○648; □746; ◇890; △942; ▽1249 h.

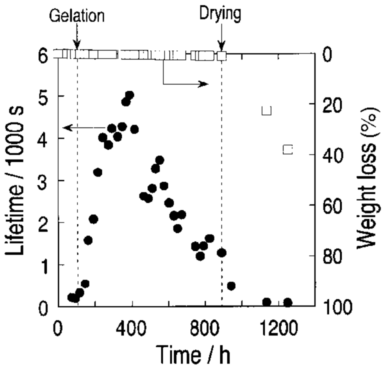

Fig. 3 Lifetime of MV^+ and weight loss of the MV-doped silica gels prepared under acidic conditions as a function of storage time at 35 °C.

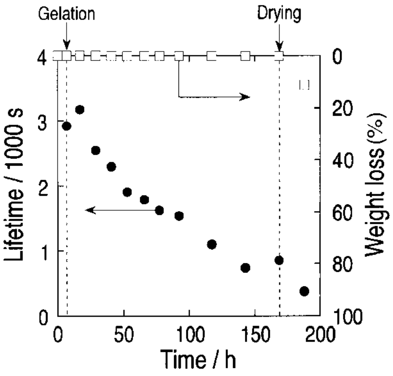

Fig. 5 Lifetime of MV^+ and weight loss of the MV-doped silica gels prepared under basic conditions as a function of storage time at 35 °C.

conditions. The values $\ln(A_t - A_0)$ on the abscissa and t on the ordinate in Fig. 4 have the same meaning as in Fig. 2. The gelation time was 6 h and the drying of the gel started at about 170 h after storage. The storage time of each gel is shown on the figure. All the plots of $\ln(A_t - A_0)$ *vs.* time for each sample are approximately linear, therefore the oxidation of MV^+ obeys first-order kinetics in gels prepared under basic conditions as well as under acidic conditions (Fig. 2). The slopes of the plots become slightly shallower from 7 to 17 h storage time (●, ■) and then become steeper as the aging process proceeds (○, □, ◇, △, ▽).

Fig. 5 shows the lifetime of MV^+ in the silica matrix and the weight loss of the MV-doped silica gels prepared under basic conditions as a function of storage time. The lifetime is the reciprocal of the slopes of the plots in Fig. 4. In the sol stage, the coloration of MV was observed after irradiation, but fading was so fast that the lifetime could not be calculated. Similarly to the gels prepared under acidic conditions, the coloration in the aging stage of the wet gels occurred only at the surface which was irradiated. The lifetime of MV^+ reaches a maximum just after the gelation point and then gradually decreases. Similarly to the gels prepared under acidic conditions, the drying was started at the time when the change in lifetime of MV^+ was hardly observed in the aging process. Consequently, it was actually impossible to calculate the lifetime of MV^+ in the gels prepared under basic conditions in the later stages ($t > 200$ h), of drying as it was for the gels prepared under acidic conditions.

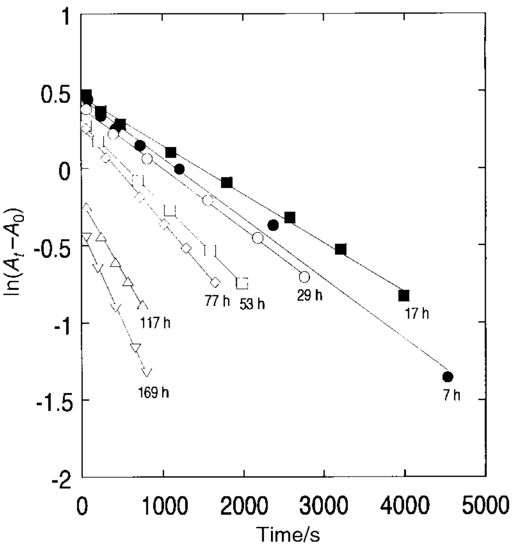

Fig. 4 Changes in the magnitude of the absorption maximum of MV^+ in the silica matrix after irradiation during the formation process of silica gels prepared under basic conditions. The values $\ln(A_t - A_0)$ on the abscissa and t on the ordinate in Fig. 4 have the same meaning as in Fig. 2. The symbols represent the storage time: ●7; ■17; ○29; □53; ◇77; △117; ▽169 h.

The lifetime of MV^+ is considered to be influenced by variations in the microscopic environment, for example, microviscosity around MV^+. In order to clarify the relation between the viscosity of the systems and the lifetime of MV^+, the lifetime of MV^+ was examined in various systems, such as water–glycerol, water–ethylene glycol and glycerol–ethylene glycol, with a variety of viscosities. Fig. 6 shows the relation between the lifetime of MV^+ and the viscosity of the solutions. The lifetime of MV^+ monotonically increases with the increasing viscosity of the solutions. These results indicate that the lifetime of MV^+ is sensitive to changes in the viscosity of the system. Solvent surrounding MV^{2+} is expected to act as an electron donor to reduce MV^{2+} to MV^+ under UV irradiation. The diffusion rates of both the generated MV^+ and the oxidized solvents surrounding MV^+ decrease with the increasing viscosity of the system, so that it is more difficult for the oxidized solvents to oxidize MV^+. Therefore, the lifetime increases with the increasing viscosity of the system.

4 Discussion

The macroscopic viscosity of sols rapidly increases in general just before the gelation point. Wet gels are macroscopically solid, but have a great deal of liquid in the network structure. MV in the gel matrix must be present in the liquid portion inside the gel. Narang *et al.* have suggested that the microenvironment around the dopant in sol–gels remains constant well beyond the gelation point.[17] The microviscosity around MV in the gel matrix prepared under acidic conditions, thus, remains low at the gelation point, and gradually increases with gel aging. The lifetime of MV^+ increases with increasing viscosity of the system, as shown in Fig. 6. The disappearance (oxidation) rate of MV^+ depends on the collision frequency of

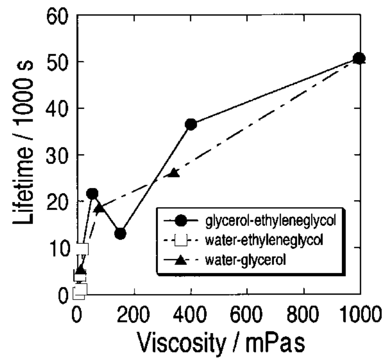

Fig. 6 Relation between the lifetime of MV^+ and the viscosity of the water–glycerol, water–ethylene glycol and glycerol–ethylene glycol solutions.

MV^+ with oxidized solvent and, thus, depends on the diffusion rates of these species. When the diffusion rates of species such as MV^+ in the sol are large, the collision frequency between MV^+ and the solvent is high. Therefore, MV^+ is easily oxidized to MV^{2+} and the lifetime of MV^+ becomes short. The lifetime of MV^+ hardly changes at the gelation point because there are no dramatic changes in microviscosity around MV^+.[17,18] After gelation, the collision frequency between MV^+ and oxidized solvent (the diffusion rates of these species) gradually decreases with increasing microviscosity around MV^+, so that the disappearance rate of MV^+ decreases, that is, the lifetime of MV^+ increases. The lifetime of MV^+ is expected to increase monotonically due to a gradual increase in the microviscosity around MV^+ with gel aging. The lifetime of MV^+, however, reached a maximum and then gradually decreased. The explanation based on the collision frequency mentioned above is valid for systems in which the diffusion rate is large, but it is not appropriate for systems in which the diffusion rate is small. In systems where the diffusion of molecules is restricted, such as in aged gels, the locations of individual MV and oxidized solvent molecules are approximately fixed in the gels. MV^{2+} accepts electrons from solvents by UV irradiation to be reduced to MV^+, but the reverse electron transfer reactions, which lead to the re-formation of more stable MV^{2+}, occur readily from MV^+ to the oxidized solvents, since MV^+ is located in the vicinity of the oxidized solvents after its formation. Therefore, the oxidation of MV^+ to much more stable MV^{2+} is facile, decreasing the lifetime of MV^+.

The lifetime of MV^+ reaches a maximum some time after the gelation point under acidic conditions (Fig. 3). On the other hand, the maximum occurs just after the gelation point under basic conditions (Fig. 5). This difference in lifetime is probably caused by the magnitude of the microviscosity around MV. The silica gel matrix prepared under acidic conditions tends to be composed of linear polymers and is thus made of fibrous particles, which are not bridged three-dimensionally so much, and is positively charged. Therefore, MV^{2+} in the pores of the particles prepared under acidic conditions should migrate readily, as in sols. On the other hand, the gel matrix prepared under basic conditions tends to consist of three-dimensionally extended polymers to form particles which are negatively charged and are condensed to each other, leading to the formation of larger particles. The silica particles with large negative charges are expected to show a strong electrostatic interaction with MV^{2+} and thus MV^{2+} should be trapped in the pores of the silica particles. As a consequence, migration of MV^{2+} in the pores of the silica particles is strongly restricted and can hardly diffuse. Therefore, under basic conditions, the lifetime of MV^+ reaches a maximum just after the gelation point. The decrease in lifetime with gel aging under basic conditions is caused by the fact that the distance between MV and oxidized solvent molecules is fixed and the oxidation of MV^+ to MV^{2+} by contact with the oxidized solvent occurs readily.

5 Conclusions

A silica gel matrix was doped with MV under acidic and basic conditions by the sol–gel method. MV-doped dry gels prepared under both acidic and basic conditions were transparent and free from cracks. The absorption peak due to MV^+ was observed at around 608 nm after UV irradiation of MV-doped silica gels under both acidic and basic conditions. The magnitude of the absorption maximum at around 608 nm gradually decreased with the passage of time after irradiation, that is, MV^+ gradually disappeared. These phenomena were also observed in solution, so that the photoredox behavior of MV in the silica gel matrix was basically the same as that in solution. The oxidation of MV^+ obeyed first-order kinetics in sols and gels under both acidic and basic conditions. The lifetime of MV^+ increased with increasing microviscosity around the MV molecules after gelation in the gels prepared under acidic conditions. The lifetime of MV^+ reached a maximum and then gradually decreased with the gel aging. This result indicates that the oxidation of MV^+ to more stable MV^{2+} readily occurred, since MV^+ was located in the vicinity of the oxidized solvent molecules due to the restriction of molecular diffusion. Furthermore, the lifetime of MV^+ in gels prepared under basic conditions reached a maximum at an earlier stage of gel aging than in gels prepared under acidic conditions. The microviscosity around MV molecules at the gelation point under basic conditions must be larger than under acidic conditions.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

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