

IRON(II)- OR VANADIUM(IV)-CONTAINING SILICEOUS GELS

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Iron(II)-containing SiO_2 gels can be prepared by the hydrolysis and condensation of tetramethoxysilane in methanolic solutions of iron(II) chloride. These gels show an absorption at 1000 nm indicating the presence of iron(II). In opposition to that, iron(II) cannot be introduced into organically modified gels of the 3-glycidylxypropyltrimethoxysilane type. Vanadium(IV) can be incorporated into both gels. Unlike the SiO_2 gels, the organically modified gels are compact and elastic. The spectra of the vanadium(IV)-containing gels show a characteristic absorption at about 800 nm. In some cases these gels change their colours with time, presumably due to the exchange of ligands in the coordination sphere of vanadium.

1. Introduction

One of the major advantages of the sol-gel process is the possibility to prepare multicomponent systems. The incorporation of cations, especially of transition metal cations, has been described by Roy [1]. This is of interest in order to obtain the special properties of the prepared materials. In conventionally melted glasses iron(II) is used for heat absorption. This is due to the absorption band at about 1000 nm, in the range of the highest total heat emission in the solar spectrum. Therefore, it should be investigated how far it is possible to introduce iron(II) into gels via the sol-gel process. Another transition metal cation to be investigated is vanadium(IV) which shows an absorption band at about 800 nm.

The basic parameters of the incorporation procedure for iron(II) as well as vanadium(IV) should be investigated with tetraalkoxysilanes as the network former. Later the use of epoxysilane $((\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{OCH}_2\overline{\text{CHCH}_2}\overline{\text{O}} = \text{glymo})$ is planned since it has been shown elsewhere that epoxysilane in connection with titanium or zirconium alkoxide leads to coatings with good mechanical properties [2,3]. For this reason, glymo was used as a network former, too. Transition metal alkoxides, especially with low valent cations, tend to be insoluble in organic solvents [4]. In this case, the introduction of soluble salts may be helpful if the anions do not create a disturbance. The objective of this paper is to investigate the basic parameters in order to prepare heat protecting materials via the sol-gel process.

2. Experimental

2.1. Preparation of iron-containing gels

Iron(II)-containing gels were prepared by dissolution of 358 mg (1.8 mmol.) $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in a mixture of 5 ml methanol and 1.2 ml water with 5 ml tetramethoxysilane. After stirring 0.5 ml of 1 N HCl was added. This leads to a homogeneous solution. Parts of the solution were directly poured into UV/VIS cuvettes of 1 cm thickness. The iron concentration was chosen to obtain measurable absorption under this condition. Gelation took place under these conditions after 24 h. The gels dried to monolithic alcohol-free products within 48 h. The absorption spectra of the gels were measured with the Hitachi UV/VIS spectrometer in the range of 200–2000 nm.

The preparation of organically modified iron-containing gels was carried out by addition of 50 mg (0.25 mmol.) $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ to a mixture of 1.1 ml methanol, 2.0 ml water and 8.3 ml glymo. After stirring 0.1 ml concentrated HCl was added. This leads to a homogeneous solution which was poured into cuvettes as mentioned above. At higher iron concentrations two phases separated.

2.2. Preparation of vanadium-containing gels

Vanadium(IV)-containing inorganic gels were prepared as described above. Therefore 50 mg (0.2 mmol.) of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ were used. In the case of vanadium-containing organically modified gels the same basic procedure as with iron was used. As catalysts 0.1 ml of concentrated HCl, H_2SO_4 or H_3PO_4 were used. Other experiments with water only were carried out in addition to this.

3. Results

3.1. Iron(II)-containing gels

Since the spectra of the dissolved transition metal salts are well-known it was of interest to compare whether the spectra change during the sol–gel transition. The spectrum of the starting solution and the spectrum after two days gelation (gel has been formed) are identical. Fig. 1 shows the spectra of the gels. An iron-free (fig. 1a) and an iron(II)-containing (fig. 1b) gel are compared with an iron(III)-containing gel (fig. 1c). The absorption band at 1000 nm is clearly observable and typical for iron(II). This is due to an octahedral coordination of the iron(II) with a magnetic normal configuration and can be attributed to the forbidden weak d–d transition. The molar extinction coefficient for the iron(II) was determined as about $3 \text{ l}/(\text{mol} \cdot \text{cm})$. The remarkable stability of iron(II) in gel derived SiO_2 glasses at a molar

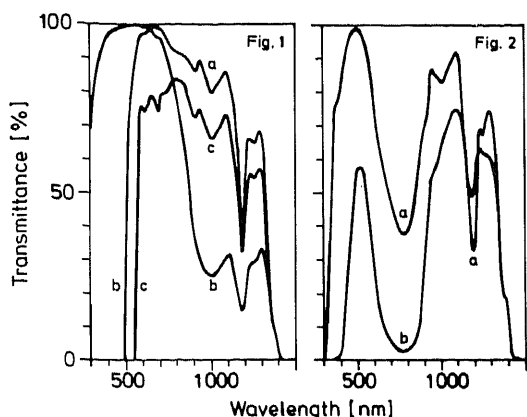


Fig. 1. Spectra of SiO_2 gels: (a) iron-free, (b) iron(II)-containing, (c) iron(III)-containing. All spectra are corrected due to scattering losses.

Fig. 2. Spectra of (a) liquid reaction mixture for a vanadium(IV)-containing SiO_2 gel, (b) vanadium(IV)-containing SiO_2 gel (not corrected due to scattering losses).

Fe/Si ratio of about 0.025 has already been reported [5]. In our case this value is about 0.05. The iron(II)-containing gel shows an IR-absorption in the range of the most intensive infrared radiation of the solar spectrum. But in order to obtain good near infrared radiation protection the material should be applicable as thick coatings, which is almost impossible with pure SiO_2 gels, especially if a dense coating is required.

Therefore, investigations were carried out to introduce iron(II) into organically modified gels. Glymo was chosen as a network forming precursor for the reason mentioned above. But in opposition to the SiO_2 gels it was not possible to avoid oxidation from iron(II) to iron(III) which was indicated by the total disappearance of the iron(II) absorption at 1000 nm. A yellow to brownish colour appears soon after mixing the iron(II) compound with the glymo, indicating that no stabilisation of the iron(II) takes place.

3.2. Vanadium(IV)-containing gels

Vanadium(IV)-containing SiO_2 gels are prepared the same way as was shown with iron(II). Fig. 2a shows the spectrum of the starting reaction mixture in the liquid phase. The mixture shows a blue colour due to a d-d transition at 770 nm. Unlike the iron-containing materials the molar extinction coefficient is 25 l/(mol · cm). Again, the spectrum of the gel (fig. 2b) does not show any difference to the reaction liquid. This indicates that the coordination sphere of the vanadium(IV) is not changed by the reaction procedure of the gelation.

In the case of the glymo gels prepared from vanadium(IV)-containing reaction mixtures (unlike the iron-containing) compact, elastic gels can be

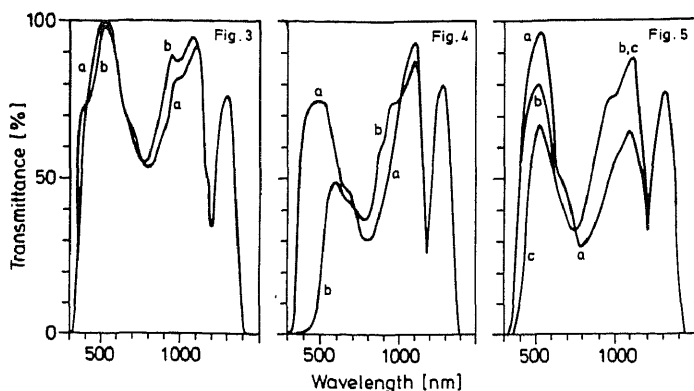


Fig. 3. Spectra of liquid reaction mixtures for vanadium(IV)-containing glymo gels: (a) with phosphoric acid, (b) with sulfuric or hydrochloric acid (or without acid).

Fig. 4. Spectra of vanadium(IV)-containing glymo gels after five days; gelation catalysed by (a) phosphoric acid, (b) sulfuric or hydrochloric acid (or without acid). All spectra are corrected due to scattering losses.

Fig. 5. Spectra of the same samples as in fig. 4 after 90 days; gelation catalysed by (a) phosphoric acid, (b) sulfuric acid, (c) hydrochloric acid (or without acid). All spectra are corrected due to scattering losses.

obtained. Even without acid as a catalyst the solid material is formed within four days. Pure glymo plus water and methanol does not condense within a month. The catalytic effect of transition metal ions in the hydrolysis and condensation of alkoxy silanes has been reported [6]. Aqueous solutions of such salts (e.g. vanadylsulfate) quite often are acidic. This may explain their catalytic effects. By adding acid (hydrochloric, sulfuric, phosphoric) to the reaction mixture, solid products are obtained within two days. In the case of phosphoric acid, gels with higher vanadium contents can be prepared (up to 30 mol.% VO_2 ; 13% by weight). Catalysis by hydrochloric or sulfuric acid leads to softer products. The solidifying effect of phosphoric acid may be explained by the fact that in contrast to chloride and sulfate ions, phosphate ions can act as a network former. If sols with suitable viscosities are used, coatings on glasses and metals with good adhesion can be prepared. The intensity of the blue colour depends on thickness and vanadium content. Phosphoric acid catalysed materials even with high vanadium content showed no change within one year at room temperature.

In opposition to this the absorption characteristics of gels catalysed by other acids differ with the type of the acid and gelling time. Fig. 3 shows the spectra of the liquid reaction mixtures for vanadium-containing glymo gels. The mixtures with sulfuric and hydrochloric acid and the mixture without acid have quite similar spectra. (fig. 3b).

With phosphoric acid (fig. 3a) a shift of the absorption band from 770 nm to 800 nm and a slight broadening is observed. The influence of the gelling

process on the absorption spectra is different. Fig. 4 shows the spectra of the gels after five days reaction time. The gel with phosphoric acid (fig. 4a) is blue like the reaction mixture and no change occurs. The gels without acid, with hydrochloric and sulfuric acid are yellow to yellow-green (fig. 4b), changing their colours with time. After about 90 days (fig. 5) the gels prepared with phosphoric (fig. 5a) or sulfuric acid (fig. 5b) are blue, gels prepared without acid or with hydrochloric acid (fig. 5c) are yellow near their surfaces and the bulk is yellow-green. All gels still show absorption bands at about 800 nm, nevertheless, whether they are yellow, green or blue. It is assumed that the change in colour is not due to a change in the oxidation state of the vanadium but to a change in the coordination sphere. The ligand in the trans-position to the short V–O bond is known to have a relatively long and weak bond to the central atom [7]. Therefore, it may easily be substituted by other ligands during the sol–gel process, like phosphate or sulfate anions, the epoxy group or alcoholic groups. During the reaction the change of the colour may be caused by the exchange of one of these ligands which may not take place in the case of the presence of phosphate ions.

4. Conclusions

The investigations show that it is possible to incorporate iron(II) and vanadium(IV) cations into gels in a cocondensation process by use of soluble salts. Iron(II) exhibits surprising oxidation stability – even in non-densified pure SiO₂ gels. The stability in glymo gels is poor. With vanadium(IV) no stability problems arise. Vanadium-containing glymo gels can be used for coatings. The cured coating, due to the absorption properties of vanadium(IV), shows heat protection qualities. For example, a 100 μm layer with 26 mol.% of VO₂ reduces the heat transmission to about 25% while the visible light transmission remains at 60%. The mechanical properties of the coatings are not sufficient for practical use so far. But the system can be used as a base for further developments for heat protecting materials.

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