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Infrared and Raman spectra of (3,3,3-trifluoropropyl)trimethoxysilane, its sol and xerogel

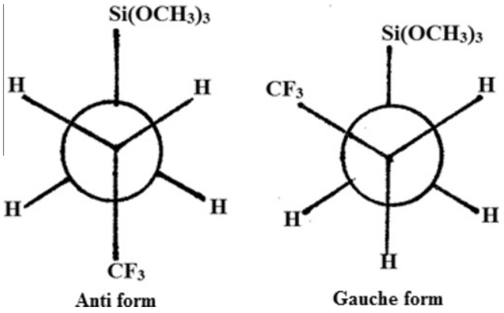
Ying-Sing Li [a,*], Nicolas E. Vecchio [a], Weijie Lu [b]

[a] Department of Chemistry, University of Memphis, Memphis, TN 38152, USA
[b] Materials and Manufacturing Directorate, AFRL/RXAN, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433, USA

HIGHLIGHTS

- ▶ TFPTMS sol and gel have been prepared.
- ▶ Two conformers were identified in TFPTMS but not in sol and xerogel.
- ▶ The progression of TFPTMS sol–gel process could be monitored with IR spectroscopic method.
- ▶ TFPTMS xerogel decomposed around 450 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic modified silica sol was prepared by using (3,3,3-trifluoropropyl)trimethoxysilane (TFPTMS) as a precursor in ethanol solution under acidic condition. Infrared and Raman spectra were recorded for the silane coupling agent (SCA), TFPTMS sol and xerogel. Vibrational assignments have been suggested based on the spectral relative intensity, results from the vibrational study of trimethoxypropylsilane (TMPS), similar trifluorocompounds and group frequencies. Low temperature IR spectra revealed the presence of two conformers in TFPTMS. Only one conformer could be identified in the TFPTMS sol and xerogel. Thermal investigation of TFPTMS xerogel with infrared spectroscopic method indicated that the organic part remained essentially unchanged at or below 350 °C but decomposed at or around 450 °C, in agreement with the result from thermal gravimetric analysis (TGA). After the decomposition of the organic branch, the remaining part of the xerogel was composed of silica.

Introduction

Silica sol–gel treatments of metal surface have shown great potential for the corrosion protection of metals. In the treatment, silica sol–gel may serve to enhance the bonding between a metal or a metal oxide surface and the external coating adhesive or paint. With an organic coating agent alkyltrialkoxysilane as the precursor in the sol–gel process, the sol–gel might provide a flexible silica film, improving the surface property of the treated metals. Our earlier studies on the sol–gel coating for corrosion protection of metals have suggested that the efficiency of corrosion protection or the corrosion inhibition efficiency depends on the choice of silyl couple agent (SCA) [1–10]. Included in the earlier studies is the use of trimethoxypropylsilane (TMPS) as a precursor [4] in the preparation of organo-modified silica sol as a metal surface modifier. Different organic groups in the organo-modified SCA are expected to generate films with different corrosion protection efficiencies. In the studies of silica sol–gel film for the corrosion protection of metals, it was pointed out the importance of hydrophobicity of the coating silica film [11,12]. (3,3,3-Trifluoropropyl)-trimethoxysilane (TFPTMS) is a trifluoro compound of TMPS in the C-3 position. Due to the presence of hydrophobic trifluoromethyl group, it would be of interest to learn how the TFPTMS sol–gel coating will

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[*] Corresponding author. Tel.: +1 901 678 2621; fax: +1 901 678 3447.
E-mail address: yingli@memphis.edu (Y.-S. Li).

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contribute to the corrosion protection of metal. In the present research, we study the infrared and Raman spectra of TFPTMS as well as its sol and xerogel, and the results are presented herein. It is expected that the results will provide some basic spectroscopic information for the anticorrosion treatment of metals in the future.

Experimental section

Materials

TFPTMS was obtained from Aldrich (Milwaukee, WI, USA) and used without further purification. Absolute ethanol was a commercial product from Aaper (Brookfield, CT, USA). Hydrochloric acid (36%) was purchased from Fisher Scientific (Pittsburg, PA, USA). The millimolar acid solution was prepared by mixing hydrochloric acid with Millipore (Bedford, MA, USA) de-ionized water, which had a resistance of 18 Mohm-cm or higher. KBr (IR grade) used for IR measurements was obtained from Sigma (St. Louis, MO, USA).

Preparation of sol and xerogel

TFPTMS sol was prepared by dropping 0.9 mL 1 mM HCl slowly into 6.1 mL of 32% (v/v) TFPTMS solution in ethanol under vigorous stirring. After the complete addition of acid, the final mixture was continuously stirred for 1 h to obtain a clear hydrosol, which had intense Tyndall effect. This homogeneous sol could be stored in refrigerator for fifty days without forming precipitation or gel. A long-time storage would cause the formation of two liquid phases. Xerogel was obtained after drying the sol at ambient condition or at 110 °C.

Infrared and Raman spectra

Infrared (IR) spectra were recorded on a Matson Polaris FTIR spectrophotometer equipped with WinFirst spectroscopic software. For collecting IR transmission spectra, a total number of 96 scans and a resolution of 2 cm^{-1} were used. Liquid sample was handled by sandwiching a drop of sample between two KBr windows, in which two KBr windows were use for background collection. For recording IR spectra of solid xerogel samples, KBr pellets were prepared by pressing 3% (by weight) of sample in KBr powder. Transmission IR spectra of solid TFPTMS was collected with a liquid nitrogen cell installed in a BioRadiate Nicolete FTIR-40 spectrophotometer. The low temperature cell is similar to the one described by Durig and his coworkers [13] in their vibrational spectroscopic studies of solids. The solid film was obtained by depositing TFPTMS vapor onto a liquid-nitrogen cooled KBr substrate through a high-vacuum system. Sample annealing was conducted by warming up the sample to a certain temperature for a reasonable time before re-cooling down with liquid nitrogen. For each spectrum collection, the number of scan was 96 and the resolution was 2 cm^{-1}.

Raman spectroscopy was performed with a Renishaw inVia spectrometer at room temperature with 514-nm laser excitation. A 50X optical microscope and about an incidence of 1–2 mW incident power at normal were used. Samples were filled in Kimax-51 capillary tubes with an inside diameter of 1.2 mm. The spectral resolution was better than 2 cm^{-1}.

Thermal gravimetric analysis (TGA)

TGA was conducted by using a Mettler TGA/SDTA851 system equipped with STARe software. Xerogel samples had been cured at 110°C before the TGA experiment. In the experiment, the heating rate was set at 10 or 5°C/min, and the heating furnace was purged with nitrogen with a flowing rate of 50 mL/min.

Results and discussion

IR and Raman spectra of TFPTMS

Raman and IR absorption spectra of TFPTMS are shown in Fig. 1A and B, respectively. The vertical lines are used to show the correspondence between the IR and the Raman peaks except their relative intensities. Most observed bands are corresponding in both IR and Raman spectra. The strongest band near 1100 cm^{-1} in the IR spectrum is contributed by the SiOC stretching vibration. In the frequency region around the strongest band, there are some strong and moderate bands attributed to CF stretch, CH_2 wag and CCC stretch. No Raman band is observable for the SiOC stretching vibration in the frequency region because of its weak Raman intensity [14]. Gruodis et al. [15] have studied the vibrational spectra of 1,1,1-trifluoropropyltrifluorosilane (TFPTFS) in different states and carried out the normal coordinate analysis by using the force constants obtained from *ab initio* calculations. TFPTMS is the substitution of three silyl fluorine atoms in TFPTFS with methoxyl groups; they have very similar structural formulas. The vibrational assignments for the trifluoropropyl group of TFPTFS should provide helpful information to the present assignments for TFPTMS. Due to the large C–F bond dipole, CF_3 stretches are expected to have intense IR bands. This is consistently true for trifluoromethyl compounds reported in literature while the corresponding Raman bands are weak [15–18]. However, the assigned vibration frequencies for the CF_3 group vary from one compound to the other. Thus additional information is needed in assigning the CF_3 vibrations. As TFPTMS is fluorination product of TMPS, of which the vibration study has been reported [4], a comparison of the observed TFPTMS bands with TMPS bands should provide useful information to assign the CF_3 vibrations. The spectroscopic study of TMPS [4] revealed that the asymmetric SiOC stretch has intense IR band but very weak Raman scattering signal, which agrees with what we observed for TFPTMS in the present spectroscopic investigation. Three strong IR bands at 1126, 1067 and 844 cm^{-1} with corresponding Raman bands unobserved, very weak and moderate intensities are assigned to the CF_3 stretches. The frequencies of these assigned vibrations are similar to those of TFPTFS [15]; no corresponding strong IR bands are observed in the IR spectrum of TMPS. As the CF_3 stretches are comparable to those of TFPTFS in both intensity and frequency, CF_3 deformation assignments are thus made based on those of TFPTFS. Due to the

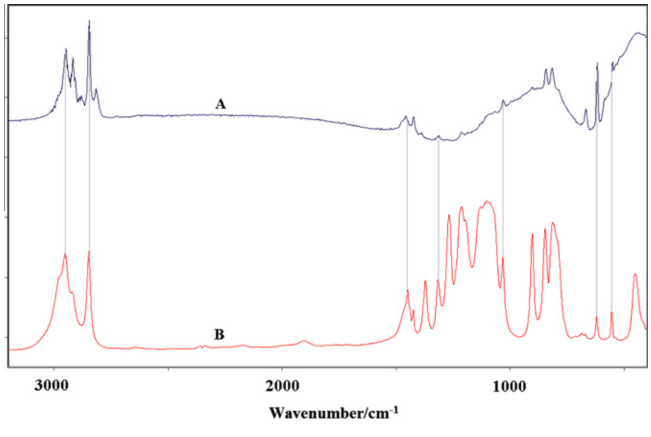

Fig. 1. Raman (A) and FTIR (B) spectra of TFPTMS.