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Structural and textural evolution of dimethyl-modified silica xerogels

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Abstract

A series of dimethyl-modified silica xerogels with different dimethyl contents were prepared by one-step hydrolysis and co-condensation from tetraethyloxysilane (TEOS) and dimethyldiethoxysilane (DEOS) containing precursor. The structural and textural evolution was traced by FT-IR spectroscopy, nitrogen absorption, scanning electron microscopy (SEM), transmittance electrical microscope (TEM), UV–Vis spectroscopy and thermogravimetric analysis (TGA). The addition of dimethyl groups can greatly reduce the pore size distribution of the resulted sample, while the 30% DEOS–70% TEOS sample is the most textural compact and therefore the most optical transparent. FT-IR and TGA results show that the samples are less hydroxygen containing owing to the hydrophobicity of the dimethyl groups.

Keywords: Structure; Texture; Dimethyl-modified; Silica xerogels

1. Introduction

Nowadays, silica xerogel has been widely used as host to incorporate different kinds of functional organic molecules for the preparation of organic/inorganic composites, which combine both the advantages of inorganic matrices and organic dopants and therefore have potential applications in many fields, such as optics, biology and catalyst [1–6]. Among which, optical functional spices/silica xerogel composites have attracted the most attention due to their very prospective applications in nonlinear optical field and optic waveguide [7–11]. However, although silica xerogel has many advantages of easy processing, high transparency and good chemical durability, it is still not a very ideal matrix for the preparation of optical composites, due to the large amounts of textural pores that existed in it, which will greatly absorb the incident irradiation energy and therefore make the composites not suitable for nonlinear optical application [12].

Up to now, several methods have been adopted for the textural improvement of porous silica xerogel. The most promising method is introduction of organic groups, for example, methyl, ethyl, vinyl, propyltrimethoxy and γ-glycidoxypropyl groups, into silica network [13–17]. The introduced organic groups do not participate in the hydrolysis and condensation reaction. Therefore they are kept unchanged during the sol–gel process and help to improve the density and flexibility of the resulted xerogels. However, to our knowledge, seldom studies have been done on dimethyl-modified silica xerogels, although they may have some special structural and textural features, owing to the equal numbers of Si–C and Si–O bonds that existed in the dimethyldiethoxysilane precursor. In this work, a series of dimethyl-modified silica xerogels with different dimethyl contents were prepared. Their structural and textural evolution was traced by FT-IR spectroscopy, nitrogen absorption, scanning electron microscopy (SEM), transmittance electrical microscope (TEM), UV–Vis spectroscopy and thermogravimetric analysis (TGA).

2. Experimental

2.1. Sample preparation

Dimethyl-modified silica xerogels were obtained by one-step hydrolysis and co-condensation of tetraethyloxysilane (TEOS) and dimethyldiethoxysilane (DEOS). DEOS (97+% purity) was bought from Aldrich. The other reagents were obtained from the

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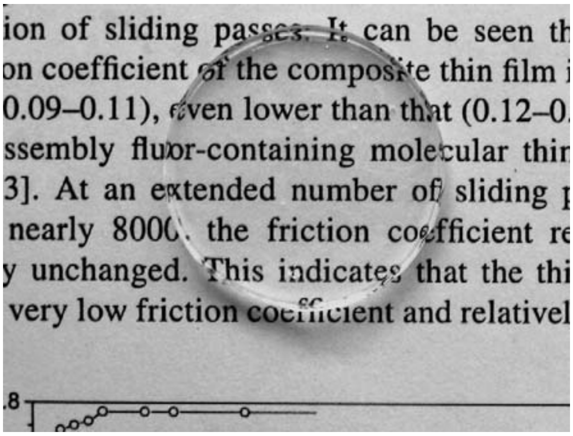

Fig. 1. A photograph of a typical dimethyl-modified silica xerogel (30% DEOS).

Chinese Regent Corporation and were of analysis grade. All the reagents were used without further purification.

The molar percents of DEOS/(DEOS + TEOS) were chosen to be 0%, 10%, 20%, 30%, 40%, and 50%, respectively. Samples with DEOS > 50% were not studied in detail because they seriously show a phase separation in the gel formation period and the resulted samples were optical opaque.

The molar ratio of (DEOS + TEOS):ethanol:distilled water in the precursor was 1:4:4. In addition, *N-N*' dimethyl formamide (DMF) was introduced in a proportion of 0.3 DMF/ethanol volume ratio, acting as both solvent and drying control chemical additive. Besides, a small amount of acid was added to the mixture to promote hydrolysis (pH = 4). After being ultrasonicated for 2 h at room temperature and becoming homogeneous and transparent, the mixture was divided into several equal volume divisions, cast into polystyrene cuvette respectively, covered with a lid, and then aging and drying in ambient environment for 2 months. When the samples were no longer weightless, the final xerogels were resulted. They were of regular circular shape with two smooth, parallel surfaces, and a unit thickness of 1 mm, which can be carried out for optical characterization without further machining (see Fig. 1).

2.2. Measurements

FT-IR spectra were recorded on a Perkin-Elmer Spectrum 2000 spectrometer. All samples were prepared in the form of KBr pellets. Pore structure of the samples was measured at 77 K by nitrogen absorption isotherm using Micromeritics ASAP 2010M Surface Area and Porosimetry Analyzer. Prior to the measurement, the samples were degassed at 120 °C for 10 h. SEM images were carried out on a JEOL JSM-6700FSEM. Gold powder was sprayed over the fresh surface of the xerogels for clearness of the images. For sample 0% DEOS, surplus TEM images were carried out on a JEM-2010 Transmission Electronic Microscope (200 kV) for the detailed characterization of the appeared smooth surface under SEM observation. UV–Vis transmittance spectra were collected on Varian Cary 50 UV–Vis spectrophotometer. The xerogels were fixed vertically in the position of silica cell by plasticene. TGA was taken on a NETZSCH STA 449C thermal analysis instrument (heating rate 10°/min, nitrogen atmosphere protection). Data in the range of 25–800 °C were collected.

3. Results and discussion

FT-IR spectra of the obtained samples are presented in Fig. 2. It shows that all the curves have a very pronounced band appearing at 1097 cm^{-1}, together with two less pronounced bands at 800 and 460 cm^{-1}, and a weak band at 550 cm^{-1}, all corresponding to the vibration absorption of Si–O–Si groups, indicating that all the samples are mainly composed of Si–O–Si network [13]. The plain band centered at 3440 cm^{-1} and the sharp band at 1670 cm^{-1} are respectively corresponding to the O–H stretching and bending absorption. Besides, there is also a small band at 960 cm^{-1} which is assigned to Si–OH vibration [13]. The intensity of these three bands consistently decreases with the increase of DEOS, due to the hydrophobicity of the dimethyl groups. In addition, there are three weak absorption bands lying at 2970, 1260, and 850 cm^{-1}, which are assigned to the absorption of Si–C vibration [13]. As expected, the

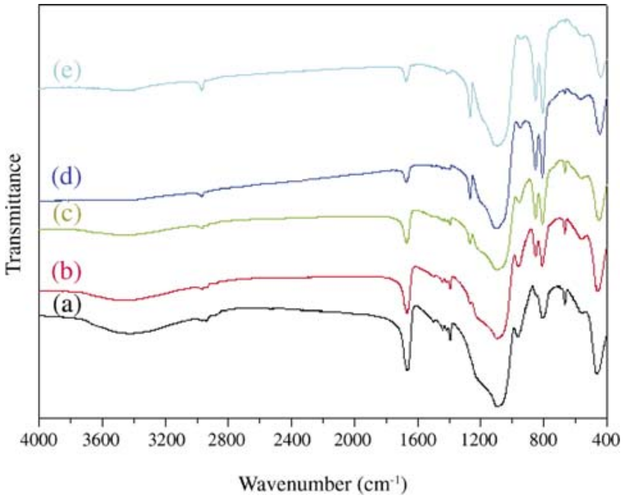

Fig. 2. FT-IR spectra of the dimethyl-modified silica xerogels. (a) 10%; (b) 20%; (c) 30%; (d) 40%; (e) 50% DEOS.

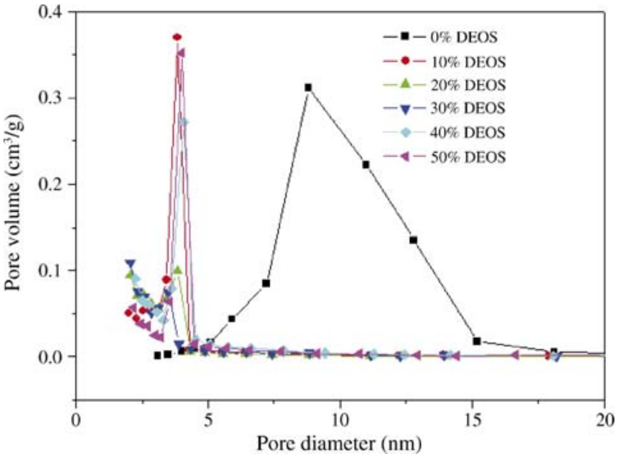

Fig. 3. Pore size distribution of the dimethyl-modified silica xerogels.