

Studies of the surface wettability and hydrothermal stability of methyl-modified silica films by FT-IR and Raman spectra

Jing Yang^{a,b}, Jierong Chen^{a,*}, Jinghua Song^b

^a School of Energy & Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

^b School of Environment & Chemistry Engineering, Xi'an Polytechnic University, Xi'an 710048, China

ARTICLE INFO

Article history:

Received 12 June 2008

Received in revised form 20 September 2008

Accepted 25 September 2008

Available online 9 October 2008

Keywords:

Surface energy

Wetting

Surface structure

Infrared absorption spectroscopy

Raman scattering spectroscopy

ABSTRACT

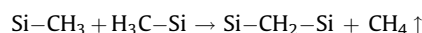
Fourier transform infrared (FT-IR) and Raman spectroscopy were employed to study the hydrothermal stability and the influence of surface functional groups on the surface wettability of methyl-modified silica films. The surface free energy parameters of the silica films were determined using the Lifshitz-van der Waals/acid–base approach. The thermal decomposition mechanisms of the CH₃ groups in the methyl-modified silica material are proposed. The results show that with the increase of methyltriethoxysilane (MTES)/tetraethylorthosilicate (TEOS) ratio, the surface free energy and surface wettability of the silica films decrease greatly. This is mainly because of the contribution of the acid–base term; the intensity of Si–CH₃ groups increases at the expense of the intensity of O–H groups in the samples. The surfaces of the methyl-modified silica films exhibited predominantly monopolar electron-donicity. The contact angle on the silica film surface reaches its maximum value when calcination is performed at 350 °C. Thermogravimetric analysis implies that some low molecular weight species, such as H₂, CH₄, and C, are eliminated upon thermal decomposition of the –CH₃ groups. The Si–CH₃ and –CH₃ vibrational bands diminish in intensity as the calcination temperature is increased, disappearing completely when the calcination temperature is increased to 600 °C. When the calcination temperature is increased to 750 °C, the free carbon and CSi₄ species will be formed.

© 2009 Published by Elsevier B.V.

1. Introduction

Silica films are unique materials with high porosities (>98%), low densities (30 kg/m³), low refractive indices (1.01–1.10), and very low thermal conductivities (<0.05 W/m²) [1,2]. Due to their fascinating properties, silica films have received significant attention in many fields, such as catalysis, adsorption, as windows for thermal and acoustic insulating systems, in anti-rust and anti-corrosive coatings, as well as in gas filtering [2–4]. They have thus found broad application in the optical, calorific, acoustic, electrical, and chemical fields. However, silica films deteriorate with time due to the adsorption of moisture from the surroundings by hydrophilic Si–OH groups present on their surfaces, which can result in the rupture of Si–O–Si bonds and pore blocking [1,5], and this limits their application. For long-term application, silica films need to have a high degree of hydrophobicity. Hydrophobicity can be increased by chemical modification and thermal treatment [6–8]. The sol–gel process is a well-established route for the synthesis

of CH₃-modified hydrophobic silica films. Over the years, a great number of scientists have been engaged in researching the synthesis and properties of hydrophobic silica aerogels and silica films [4,8–12]; however, they have not explicitly expressed the reasons for the surface hydrophobicity of the silica particles. Moreover, the surface structures of silica films have only been characterized by their FT-IR spectra [4,13–16]. Raman spectra of silica films have only rarely been reported to date. Especially, there was no in-depth research report on the thermal decomposition of the –CH₃ groups in methyl-modified silica material. The mechanism about the pyrolysis of methyl-modified silica material was not clear. Renate et al. [8] surmised that, by calculating the weight loss from the methyl-modified silica material, there should be –CH₂–group formation in the thermally induced condensation of methyl groups which was likely to occur in a reaction such as



Unfortunately, they did not find the direct evidence of –CH₂ group formation and did not propose the integrated decomposition mechanism of the methyl groups in the MTES-modified silica material.

* Corresponding author. Tel.: +86 29 82665347.

E-mail address: jrchen@mail.xjtu.edu.cn (J. Chen).

In this paper, the influences of the methyltriethoxysilane (MTES)/tetraethylorthosilicate (TEOS) ratio on the hydrophobicities of the methyl-modified silica films are reported. The surface free energies and the components thereof have been calculated for the MTES-modified silica films based on the Lifshitz-van der Waals/acid–base approach [17–19]. The effect of interface–molecule interaction forces on surface wettability is discussed. The surface structures and thermal stabilities of MTES-modified silica films have been analyzed by FT-IR and Raman spectroscopies.

2. Experimental

2.1. Silica sol preparation

The silica sols were prepared by acid-catalyzed hydrolysis and condensation of TEOS and MTES in ethanol. The complete sol preparation procedure was as follows: according to the calculated molar ratio, a mixture of HNO₃ and water was carefully added dropwise, using a dropping funnel, to a mixture of TEOS and absolute ethanol under vigorous stirring. The reaction mixture was then mechanically stirred with water reflux for 3 h at 70 °C. The molar ratios of the sol compositions were TEOS/MTES/EtOH/H₂O/HNO₃ = 1/X/7.6/7.2/0.085, where X was 0, 0.3, 0.5, 0.8 and 1.0, respectively. Each reaction mixture was subsequently cooled and diluted threefold with absolute ethanol to obtain the final dip solutions.

2.2. Silica film preparation

Dense α-Al₂O₃ ceramic plates (of dimensions 20 mm × 20 mm × 1.5 mm) were used as substrates for the preparation of silica films. The silica films were prepared by dip-coating a substrate in a diluted silica sol, followed by drying and calcining. After dipping, the films were dried at room temperature for 3 h and calcined at 105–750 °C for 2 h in air at a heating rate of 0.5 °C/min and a cooling rate of 1 °C/min. The whole process of dip-coating, drying, and calcining was repeated once more to repair any defects that there might have been in the first silica film layer. 30 cm³ of threefold ethanol-diluted silica sol was allowed to evaporate in a 9 cm diameter Petri dish at room temperature so that thin silica gel flakes were obtained. Unsupported silica materials were prepared from the gel flakes by the same calcination procedure as described above, which were made for characterization by means of FT-IR, Raman spectra and thermogravimetric analysis (TGA).

2.3. Characterization

Contact angle measurements were performed using a contact angle meter (JY-82 contact angle analyzer, Chengde, China) to quantify the degree of hydrophobicity. 10 μL liquid droplets were placed at ten different sites on the surface of the silica film. The contact angle was measured for each; the average value and standard deviation were taken.

According to the Dupre equation [20]:

$$W_a = \gamma_s + \gamma_L - \gamma_{SL} \quad (1)$$

where the energy of adhesion (W_a) is directly related to the surface free energy of the two adjacent phases S (film) and L (liquid). Therefore, lower adhesion corresponds to lower surface free energy.

According to the van Oss–Chaudhry–Good (vOCG) theory, the surface free energy, γ^T , consists of an apolar Lifshitz–van der Waals component, γ^{LW} (which comprises the dispersion, as well as the induction and orientation contributions to the van der Waals

interactions) and a polar Lewis acid–base component, γ^{AB} , such that

$$\gamma^T = \gamma^{LW} + \gamma^{AB} \quad (2)$$

where γ^{AB} is the geometric mean of the electron-donor (γ^-) and electron-acceptor (γ^+) parameters for the applied liquid or the substrata, given by

$$\gamma^{AB} = (\gamma^+ \gamma^-)^{1/2} \quad (3)$$

When a drop of a liquid is deposited on a solid surface, the contact angle between the drop and the surface (θ) is a function of the components and parameters of the surface tensions of the liquid and the solid. The Young–Dupré equation relates such magnitudes [17–19]:

$$\gamma_L^T (1 + \cos \theta) = 2(\gamma_s^{LW} \gamma_L^{LW})^{1/2} + 2(\gamma_s^+ \gamma_L^-)^{1/2} + 2(\gamma_s^- \gamma_L^+)^{1/2} \quad (4)$$

Thus, by contact angle (θ) measurement with three different liquids (of which two must be polar) with known γ_L^{LW} , γ_L^+ and γ_L^- values. We resolve the following system:

$$\gamma_{L1}^T (1 + \cos \theta_1) = 2(\gamma_s^{LW} \gamma_{L1}^{LW})^{1/2} + 2(\gamma_s^+ \gamma_{L1}^-)^{1/2} + 2(\gamma_s^- \gamma_{L1}^+)^{1/2} \quad (5)$$

$$\gamma_{L2}^T (1 + \cos \theta_2) = 2(\gamma_s^{LW} \gamma_{L2}^{LW})^{1/2} + 2(\gamma_s^+ \gamma_{L2}^-)^{1/2} + 2(\gamma_s^- \gamma_{L2}^+)^{1/2} \quad (6)$$

$$\gamma_{L3}^T (1 + \cos \theta_3) = 2(\gamma_s^{LW} \gamma_{L3}^{LW})^{1/2} + 2(\gamma_s^+ \gamma_{L3}^-)^{1/2} + 2(\gamma_s^- \gamma_{L3}^+)^{1/2} \quad (7)$$

The γ_s^{LW} , γ_s^+ , and γ_s^- of any solid can be determined. In this case, three liquids (distilled water, formamide, α-bromonaphthalene) were used to determine γ_s^{LW} , γ_s^+ , and γ_s^- of these films. The parameters of the probe liquids used in measuring the contact angle of the silica films are given in Table 1.

FT-IR spectra were obtained by a Nicolet 5700 spectrometer from 400–4000 cm⁻¹. The spectral resolution was 1 cm⁻¹ and the collection time was about 1 min. The samples were pressed into KBr pellets. Raman spectra were recorded at room temperature on a Renishaw Invia Raman microscope. The wavenumber range covered was 200–3200 cm⁻¹ and the spectral resolution was 1 cm⁻¹. Thermogravimetric analysis was performed on non-calcined unsupported silica materials by a TGA/SDTA851^e with a heating rate of 5 °C/min to 800 °C in air. Atomic force microscopy (AFM) measurements were carried out using a Nano Scope IIIa microscope from Digital Instruments, USA.

3. Results and discussion

3.1. FT-IR analysis

There is a close relationship between the composition and the quantity of the characteristic functional groups in the sample. The FT-IR spectra of silica films with MTES/TEOS = 0, 0.3, 0.5, 0.8 and 1.0 calcined at 400 °C were shown in Fig. 1. In Fig. 1, the bands at 1053, 790 and 443 cm⁻¹ are associated with the Si–O asymmetric stretching, Si–O symmetric stretching and Si–O–Si bending vibrations, respectively. The band at 940 cm⁻¹ is due to the O–H stretching vibration in Si–OH group. The bands at 3450 and

Table 1

Surface free energy parameters (mJ/m²) of the liquids at 20 °C used for contact angle determinations.

Liquid	γ^{LW}	γ^+	γ^-	γ^{AB}	γ_L^T
Distilled water	21.8	25.5	25.5	51.0	72.8
Formamide	39.0	2.28	39.6	18.3	57.3
α-Bromonaphthalene	44.4	0.0	0.0	0.0	44.4

Download English Version:

<https://daneshyari.com/en/article/1252105>

Download Persian Version:

<https://daneshyari.com/article/1252105>

[Daneshyari.com](https://daneshyari.com)