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Surface modification of nanosilica with 3-mercaptopropyl trimethoxysilane: Experimental and theoretical study on the surface interaction

Jianbing Wu [a,b], Lixia Ling [c], Junbao Xie [d], Guozhang Ma [b], Baojun Wang [a,*]

[a] Key Laboratory of Coal Science and Technology, Taiyuan University of Technology, Ministry of Education and Shanxi Province, Taiyuan 030024, China
[b] Shanxi Research Institute of Applied Chemistry, Taiyuan, Shanxi 030027, China
[c] Research Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China
[d] College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China

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ABSTRACT

Surface modification of nanosilica with 3-mercaptopropyl trimethoxysilane (MPTMS) has been investigated. FTIR, TGA, CA, ^{29}Si NMR and DFT method have been applied to study the interaction between nanosilica and MPTMS. The results show that the organic functional groups are successfully grafted onto the nanosilica surface and the grafting ratio firstly increases and then decreases with the increasing MPTMS. In addition, four different grafting modes between nanosilica surface and MPTMS have been studied by DFT method. It indicated that the favorable grafting structures are mono-, di-grafting mode when the MPTMS is lower and ladder-like grafting mode when the MPTMS is higher.

1. Introduction

There have been increasing activities in the development of organic–inorganic hybrid material in recent years, especially the incorporation of inorganic nanoparticles into organic coatings and other polymers matrix [1–4]. Nanosilica has attracted enormous attention for its high abrasion resistance, hardness and scratching resistance in the photocurable coatings [5–7]. However, the nanosilica tends to strongly agglomerate due to the large surface-area/particle-size ratio, which reduces the resultant mechanical properties of the hybrid material [8]. Many physical and chemical efforts have been done to overcome this problem and to enhance organic–inorganic phase interaction.

Different silane coupling agents for surface modification of nanosilica is recommended to achieve proper dispersion of nanosilica in polymer matrix and to yield a better compatibility between nanosilica and host polymers [9–11]. Usually, the silane coupling agents undergo stepwise hydrolysis reactions in a mixture of water/ethanol leading to the formation of silanol units, which can reacts with hydroxyl of nanosilica surface not only to form Si–O–Si but also hydrogen bond O···H–O [12]. The influences of temperature [13], solvent [14], concentration [15] and pH [12] on the hydrolysis of different silane coupling agents have been investigated during the modified nanosilica preparation. However, the grafting mechanism and the grafting situation (or mode) of silane coupling agent onto the nanosilica surface are still not clear.

Recently, the theoretical calculation method has been applied to confirm the interaction between small molecule or radical group and nanosilica [16]. The silica cluster with different structure from $Si_2O_3H_4$ to $Si_{12}O_{14}H_{24}$ have been comprehensively used to study the interaction between silica and different molecular structure, including CH_3 [17], HF [18], trihydroxysilane, trichlorosilanes [19], triethoxysilane and bis (3-triethoxysilylpropyl)-tetrasulfane [20]. The hydroxyl groups of the hydrolyzed silane interacts to the cluster in one way with a strong covalent bond Si–O–Si, and in the other way to the cluster by moderated hydrogen bond O···H–O. It shows that the Si–O–Si bond length and strength are different with the different silane coupling agents onto the silica cluster [21]. However, the detail information of bonding pattern and situation, the priority between hydrolysis, self condensation of silane coupling agent and grafting is unclear. Recently, calculations were also carried out on the fully and partially hydrolyzed products of silane, and the good model for frequencies of the SiO/SiC symmetric stretching vibrations was provided [22].

Considering the complexity of silanol structure of hydrolyzed silane coupling agent and diversity of hydroxyl on the nanosilica surface, it is very essential and helpful to conduct a systematic and theoretical study on the interaction between silane coupling agent and nanosilica surface. In this study FTIR, TGA, ^{29}Si NMR and CA were used to characterize the grafting effect, and the DFT theoretical calculation was used to study the grafting mode of

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* Corresponding author. Address: No. 79 Yingze West Street, Taiyuan 030024, China. Fax: +86 351 6041237.

E-mail addresses: wangbaojunwork@hotmail.com, wujianbin_1982@126.com (B. Wang).

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silane coupling agent 3-mercaptopropyl trimethoxysilane (MPTMS) onto nanosilica surface.

2. Experimental

2.1. Materials

Nanosilica powder with an average particle size of 20–50 nm, a specific surface area of 640 m^2/g and silanol group content of 1.9 mmol/g was obtained from Zhejiang Hongsheng Materials Co., China. 3-mercaptopropyl trimethoxysilane (MPTMS) was purchased from Sigma Chemical Co. and was used as coupling agent. All other chemicals were analytical pure reagents (AR) and were used as received without further treatment.

2.2. Surface modification of nanosilica with MPTMS

10 g of nanosilica were kept in a vacuum chamber for 24 h at 100 °C, and then dispersed in 150 mL anhydrous toluene under mechanical stirring and ultrasonic dispersing for 30 min. The mixture was stirred at 300 rpm for a further 1 h, and then dropped into another prepared mixture consisting of 10 mL water, 10 mL anhydrous ethanol, 2 mL formic acid (as pH adjuster) and different levels (25, 50, 75, 100 and 125 mL) of MPTMS under vigorously stirring. After continuously stirring for 4 h at 50 °C, the obtained suspension was separated by centrifugation. After drying at 90 °C under vacuum, the mixture was extracted using Soxhlet extractor for 12 h using toluene. Finally, the modified nanosilica was dried at 90 °C under vacuum condition for 12 h.

2.3. Characterizations

The mercapto group on the nanosilica surface was determined with the DTNB according to the method of Ellman [23]. FTIR analysis was performed in potassium bromide on a Nicolet 360 FTIR spectrometer collecting 16 scans in the 400–4000 cm^{-1} range with 4 cm^{-1} resolution. The thermo gravimetric analysis (TGA) was performed on a HCT-1 thermal gravimetric analyzer (Henven Scientific Instument Co., China) under a nitrogen atmosphere from room temperature to 700 °C with the heating rate of 20 °C/min. The grafting ratio (R_g) was calculated according to the following equation [24]:

$$R_g = \left(\frac{W_1}{W_1'} - \frac{W_0}{W_0'} \right) \times 100\%$$

where, W_1 is the starting weight of the modified nanosilica particles, W_1' is the residual weight of the modified nanosilica particles at 700 °C, W_0 is the starting weight of unmodified nanosilica particles, W_0' is the residual weight of unmodified nanosilica particles at 700 °C.

The particle (or particle agglomeration) size and the distribution of nanosilica before and after modification were characterized by a laser particle analyzer Bettersize 2000 (Dandong Bettersize Instruments Corporation, Dandong, China). Ethanol was used as the following liquid.

The water contact angles (CA) was measured with deionized water drops on the nanosilica surface pellet, which was obtained by compacting nanosilica powder with 100 kN force. The measurement was carried out within 10 s by a Krüss contact angle instrument (Easydrop DSA 20) at room temperature using the sessile drop fitting method for the static CA.

Solid-state ^{29}Si MAS NMR measurements were performed on a Brucker DMX 600 spectrometer. A pulse repetition time of 2.0 s, an acquisition time of 20.0 ms, a contact time of 10.0 ms, and a frequency of 59.582 MHz were used.

2.4. Quantum chemistry calculations

The density functional theory (DFT) calculations are performed within the Materials Studio software developed by Accerlys Inc. [25]. The structure is fully optimized without any structural restrictions within the functional of generalized gradient approximation (GGA) proposed by Perdew and Wang (PW91) [26,27], which is generally used to study the structures and energies of SiO_2 with different clusters [28,29]. The DNP basis set, which is equivalent in accuracy to the 6-31G** GAUSSIAN orbital basis set, is also used [30]. The solvent effect is investigated using the conductor-like screening model (COSMO) according to the experimental reaction condition. The calculated O–H distance in 8T (tetrahedral) silica cluster is about 0.97 Å, which is in good agreement with the literature [17]. The Si–O bond lengths are about 1.64 Å and Si–O–Si angles are in the range of 143–150°. The hydrolyzed MPTMS is chose as reactant with four different grafting modes onto the silica cluster surface.

3. Results and discussion

3.1. Surface modification of nanosilica and characterization

Figure 1 shows the FTIR spectrums of nanosilica, modified nanosilica and MPTMS. In Figure 1a, the peak at 2570 cm^{-1} corresponds to the –SH groups of MPTMS, the vibration bands at 2926 and 2855 cm^{-1} relate to the symmetric and asymmetric stretching of $–CH_2$, which is observed in the vibration spectra of modified nanosilica (Figure 1c–g). It indicates that the long alkyl chain has been grafted onto nanosilica surface, and the peak strength firstly increases and then decreases with the increasing amount of MPTMS. From the FTIR spectra of nanosilica, the presence of adsorbed water and free surface silanol groups as well as siloxane linkages can easily be conceived. In the spectra, the broad band located in the range 3000–4000 cm^{-1} corresponds to the fundamental stretching vibration of different hydroxyl groups, and the Si–OH group at 3750 cm^{-1} is covered by the broad bands at 3451 cm^{-1} corresponding to the associated water vapor on the nanosilica surface. While the asymmetric stretching vibration is near 810 cm^{-1}, the symmetric stretching vibration and bending vibration is near 470 cm^{-1} of Si–O–Si (Figure 1b). From Figure 1c–g, The strength of peak at 3430 and 1650 cm^{-1} decrease and Si–O–Si at 1100 cm^{-1} increases with the increasing amount of MPTMS. However, the appearance of peak at 950 cm^{-1} of modified nanosilica

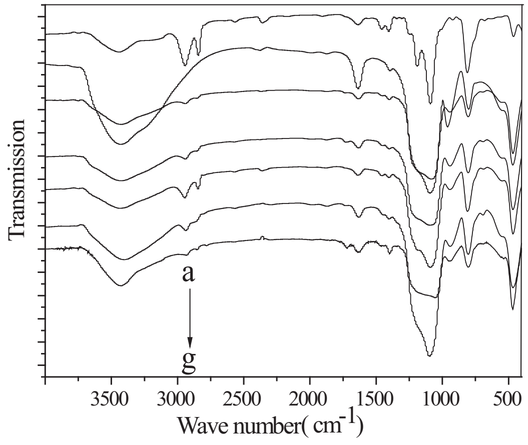

Figure 1. FTIR spectra of (a) MPTMS, (b) nanosilica, and modified nanosilica with different amounts of MPTMS, (c) 25 mL, (d) 50 mL, (e) 75 mL, (f) 100 mL and (g) 125 mL.