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# Effect of solvent polarity and adsorbed water on reaction between hexyltriethoxysilane and fumed silica

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HIGHLIGHTS

- Effects of solvent polarity on surface modifier density of fumed silica were investigated.
- Aside from solvent polarity, solubility of modifier in solvents affects surface modifier density.
- Relationship between amount of adsorbed water at silica surface and solvents should be considered.

GRAPHICAL ABSTRACT
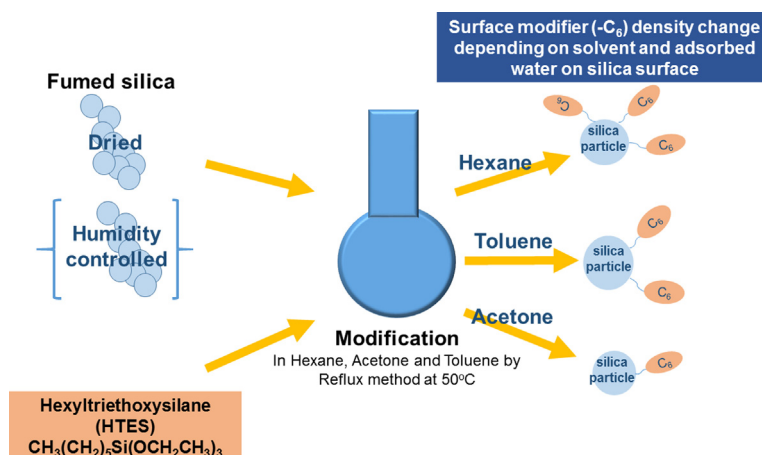
ABSTRACT

The effects of a solvent on the surface modification progress of fumed silica were investigated. Hexane, toluene, and acetone as the reacting solvent and hexyltriethoxysilane as the surface modifier were used. After a 1 h reaction at 50 °C, the surface modifier density was calculated from the weight loss of the reacted modifier at the silica surface. With a decrease in the solvent polarity (in the order of acetone, toluene, and hexane), the surface modifier density increased. Hexane and toluene have similar solvent polarities. However, behavior of the surface modifier density as a function of the modifier amount was totally different. By considering the solubility of the modifier in the solvents, hexane has a higher solute ability for the modifier than toluene. The reaction between the modifier and silica was promoted in hexane, but not promoted in toluene. In addition to the solvent property, adsorbed water on the silica surface is important for the reaction. In hexane and toluene, the amounts of adsorbed water at the silica surface showed the maximum surface modifier density of about 30 mg and 50 mg, respectively. It can be postulated that the adsorbed water layer could be fixed in hexane while diffused in toluene. Based on these results, it can be concluded that the solvent polarity, solubility of the modifier, and adsorbed water amount at the silica surface should be considered in order to achieve the desired surface modification.

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1. Introduction

Nano-sized fumed silica has been widely used in many fields, such as cosmetics [1,2], CMP and electronics [3], sealants and

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adhesives [4–6], paints and coatings [7–10], silicone rubber [11], toners [12], etc., to improve their functionalities. For these applications, dispersion of the fumed silica in the desired medium, such as organic solvents, polymers, water, etc., is required. However, aggregation of the fumed silica easily occurs, induced by many hydrophilic silanol (SiOH) groups on the silica surface [13]. To obtain such a desired dispersion in organic solvents, affinity control between the silica surface and solvent is effective through surface modification using a modifier such as silane coupling agents and alcohols [14,15].

Silane coupling agents mostly have one functional group with various physico-chemical properties such as hydrophobic, hydrophilic, polar, non-polar, etc. The other groups are alcoxyde (OR) which turns into SiOH via hydrolysis in the presence of water then forms hydrogen bonds with the SiOH of the silica surface. The functional groups of the modifier should be suitable for the organic solvent. The methods to induce a reaction between these modifiers and the silica surface can be categorized into a gas phase [16,17], liquid phase [17,18], and autoclaving [19]. In the liquid phase, the modifier was dissolved in the selected organic solvent. Hydrolysis and condensation are then induced and progress by heating or the addition of a catalyst [20].

In the liquid phase reaction, the surface modification process can occur as follows.

a) Hydrolysis of modifier occurs with water to form the SiOH group.
b) The hydrolyzed modifier forms hydrogen bonds between its SiOH and the SiOH of the silica surface.
c) Dehydration between SiOH provides the covalent bond.

In reaction (a), the water necessary for the hydrolysis of the modifier can be adsorbed at the silica surface; reaction (b) depends on the stability of the modifier-adsorbed silica in the reaction solvents; and reaction (c) is promoted by heating or a catalyst. The progress of reaction (b) could be dominated by the physical properties of the selected solvents such as their polarity, solubility of the modifier, etc.

As a reacting solvent for surface modification via the liquid phase, hexane and toluene are often utilized [21,22]. These solvents are chemically stable so that there is a low probability to limit the reaction between the modifier and silica surface.

For hydrolysis of the modifier, only a small amount of water, which is at least equivalent molar to the modifier, was necessary. As the silica surface has many SiOHs, a certain amount of water chemically and physically adsorbs which can be controlled by the relative humidity [23]. In hexane and toluene, the adsorbed water on the silica surface could be useful for hydrolysis because extra water in the atmosphere is not going into these hydrophobic solvents. The hexane and toluene seem to be definitely effective reacting solvents for the surface modification, however, the different progress of the reaction between the modifier and solvents has never been investigated in terms of their physical properties.

In this study, the effect of the solvents on the surface modification progress was investigated. As the dispersed silica, fumed silica was chosen because of its nonporous and the surface smoothness. Hexane and toluene were used as low polar solvents. As a comparison, acetone was used as a high polar solvent. The relative permittivity was used as an index of the solvent polarity. Hexyltriethoxysilane was used as a modifier. In addition, the relationship between the amount of adsorbed water at the silica surface and in the reacting solvent was investigated and the optimum water amount was determined for the surface modification.

2. Experimental

2.1. Materials

Hexane (Hex), toluene (Tol), and acetone (Ace) of special chemical grade (Wako Pure Chemical Industries, Ltd.) were used as organic solvents after overnight removal of the dissolved water by dried molecular sieves (3A Wako Pure Chemical Industries, Ltd.). Fumed silica powder was supplied by Nippon Aerosil Co., Ltd., as Aerosil200 (abbreviated A200) with the specific surface area of $200\,m^2/g$ calculated by applying the Brunauer–Emmett–Teller (BET) equation [24] to the nitrogen adsorption isotherms. To adjust the amount of water adsorbed on the A200 surface, the A200 was dried under reduced pressure at $180\,°C$ for 2 h then the A200 was exposed to the various relative humidities (RH) of 42.8, 68.8, and 92.0% for one week at $25\,°C$ by the corresponding saturated salt solutions of K_2CO_3, KI, and KNO_3 (Wako Pure Chemical Industries, Ltd.), respectively [25–28]. The amounts of water at for 2 g of the A200 surface were determined to be as 30, 50, and 190 mg, respectively. As a the surface modifier agent, hexyltriethoxysilane (HTES, $CH_3(CH_2)_5Si(OCH_2CH_3)_3$, Tokyo Chemical Industry Co., Ltd.) with a hydrophobic chain was used.

2.2. Surface modification

The A200 (2.0 g) samples with the controlled adsorbed water were dispersed in the dehydrated solvents (150 ml) containing 0.3–4.2 ml/g of dissolved HTES. The suspensions were stored at $50\,°C$ for 1 h. The treated A200 samples were separated by centrifugation and dried under reduced pressure at $80\,°C$ for 2 h.

2.3. Characterizations

How many $CH_3(CH_2)_5Si$ ($-C_6$) groups of HTES introduced on the A200 surface was determined using thermogravimetric and differential thermal analysis (TG-DTA, Thermo Plus 8120, Rigaku Co., Ltd.) as shown in Fig. 1. The measurement was carried out under air. The value was calculated from the deference in the weight loss between modified sample (W_{CH}) and unmodified sample (W_{OH}). Described as the surface HTES density were determined by the following Equation (1) [29,30].

$$d_A\left(\frac{-C_6}{nm^2}\right) = \frac{(\Delta W_{CH} - \Delta W_{OH})N_A}{M_W S_{N2}} \times 10^{-18} \tag{1}$$

where d_A is the surface density ($-C_6/nm^2$), M_w is the the molecular weight of the modifier, S_{N2} is the BET specific surface area measured from the nitrogen adsorption isotherm, and N_A is Avogadro's number. ΔW_{CH} and ΔW_{OH} are the weight loss of the modified and unmodified A200 measured by thermogravimetric and differential thermal analyse, respectively.

3. Results and discussion

To investigate the effect of the solvent polarity on the surface HTES density, the A200 sample with 30 mg of adsorbed water was treated in each solvent at $50\,°C$ for 1 h. The relative permittivities ($\varepsilon/\varepsilon_0$) of Hex, Tol, and Ace were 1.88, 2.38, and 20.7, respectively [32,33]. Fig. 2 shows the surface HTES density as a function of the added amount of HTES from 0.3 to 4.2 ml/g in (a) Hex, (b) Tol, and (c) Ace. In the order of Hex, Tol, and Ace (i.e., with an increase in $\varepsilon/\varepsilon_0$), the surface HTES density increased. In Hex, the surface HTES density was almost constant at about 0.3 ($-C_6/nm^2$) for the amount of HTES, while in Tol, it increased with an increase in the HTES amount. In Ace, it showed a low and constant value of about $0.1/nm^2$.

Ace is a polar solvent, therefore, the reaction between HTES with the non-polar C_6 group and the polar A200 surface is not promoted