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Control of hydroxyl group content in silica particle synthesized by the sol-precipitation process

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Abstract

This study investigated the control of hydroxyl groups, one of key factors determining the surface properties of silica particles synthesized by the sol-precipitation of tetraethyl orthosilicate (TEOS). Thus, a thermal gravity analysis (TGA) was used to facilitate quantitative measurements of the hydroxyl groups on the silica particles, while BET and FT-IR were used to analyze the specific surface area and functional silane groups on the silica particles, respectively. In the sol-precipitation process, silanes that include various hydroxyl groups are formed as intermediates based on the hydrolysis and condensation of TEOS. Thus, NH_3, as a basic catalyst initiating the nucleophilic substitution of TEOS, was found to accelerate the hydrolysis and increase the hydroxyl group content on the silica particles. Plus, the hydroxyl group content was also increased when increasing the concentrations of TEOS and water as the hydrolysis reactants. However, the hydroxyl group content was reduced when increasing the temperature, due to the promotion of condensation. Based on the weight loss of the particles according to the thermal analysis, the hydroxyl group content on the silica particles varied from 5.6–42.7 OH/nm^2 under the above reaction conditions.

Keywords: Hydroxyl groups; Hydrolysis; Condensation; Silica particle; Surface property

1. Introduction

The adsorption, adhesion, chemical, and catalytic properties of silica particles depend on the chemistry of the particle surface. Thus, since the surface activity of silica particles as an oxide adsorbent is directly determined by the concentration and distribution of hydroxyl groups (silanol) on the silica surface, the surface chemistry of silica has become a serious focus of study for many practical applications.

Hydrolysis and condensation are the most common processes used to synthesize silica particles. In the case of synthesizing silica using TEOS, the silica is produced based on the consecutive use of hydrolysis and condensation, where silicon hydroxides (silanols) are formed by hydrolysis and then turned into silica by water condensation. Yet, the persistent presence of hydroxyl groups on silica particles has also been established due to the incomplete condensation of silanols during the synthesis process of silica [1–4]. According to De Farias and Airoldi [5] and the Niinistö group [6], three types of hydroxyl group, including isolated silanols, germinal, and vicinal silanols, would appear to exist in silica particles, as confirmed by thermal gravity analyses. Plus, Zhuravlev's method using a mass spectrometer has been used to distinguish the hydroxyl groups on the surface and in the body [7,8], and NMR and IR used to identify the hydroxyl groups in silica particles [9].

Meanwhile, hydroxyl groups have been found to play a key role when coating silica particles with polymers and titania (TiO_2) [10–12]. For example, the UV-induced radical graft polymerization of methyl methacrylate (MMA) on silica particles has been shown to be practically initiated at the sites of hydroxyl groups, resulting in the formation of a chemical bonding between PMMA and silica [10,11]. A similar result was also obtained when coating silica particles with titania,

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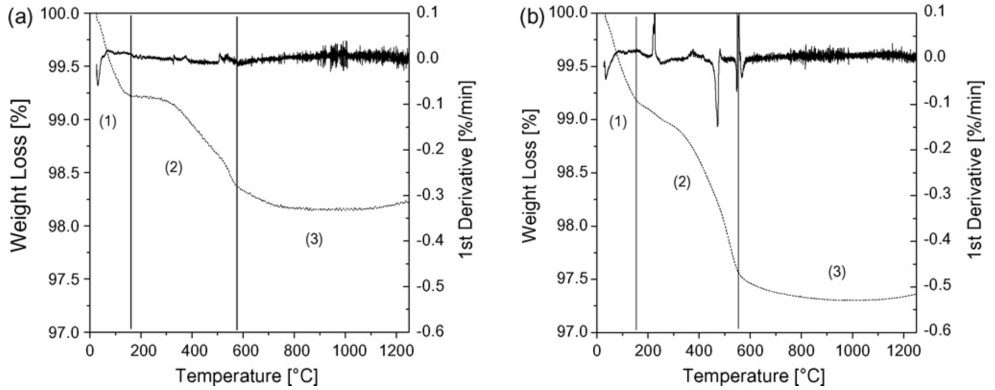

Fig. 1. TG and DTG curves for silica particles scanned at heating rate of 5 °C/min in dynamic argon atmosphere: (a) H_2O 4.88 mol/l and (b) H_2O 8.88 mol/l. The TEOS and ammonia concentrations were fixed at 0.6 mol/l and 2.0 mol/l, respectively, and the temperature set at 25 °C. (1) Dehydration: 100–130 °C, (2) dehydroxylation of germinals and vicinals: 200–600 °C, and (3) dehydroxylation of isolated silanols: above 600 °C.

where the TiO_2 was synthesized by the hydrolysis and condensation of TBOT (tetra butyl orthotitanium) and deposited on the silica particles. Here, the titanium hydroxides were partially condensed with the hydroxyl groups on the silica particles, forming a nano-scale layer of titania. The chemical binding of the titania and silica was confirmed as Si–O–Ti based on FT-IR and XPS [12].

However, relatively few studies have attempted a quantitative investigation of the hydroxyl groups on silica particles during the synthetic process as a means of controlling the surface properties of silica particles. Accordingly, the present study focused on developing a method to control the hydroxyl group content on silica particles by adjusting the synthetic conditions of sol-precipitation. As the sol-precipitation process consists of the hydrolysis and condensation of TEOS, the concentrations of TEOS, NH_3, and water and the reaction temperature were investigated as the key factors controlling the hydroxyl group content of the silica particles.

2. Experiment

Based on the Stöber method, silica particles were synthesized with TEOS in a standard Rushton reactor (working volume of 430 ml) equipped with a stainless steel six-paddle turbine impeller and four baffles for turbulent mixing [13]. Initially, a 330-ml mixture of methanol (ACS grade, Fluka, Swiss) and ammonium hydroxide (ACS grade, Sigma–Aldrich, U.S.A.) was loaded in the reactor. A 100-ml TEOS (ACS grade, Fluka, Swiss) solution was then fed into the reactor at a flow rate of 1.92 ml/min using a syringe pump. To modify the synthetic conditions of the silica particles, the TEOS, water, and ammonia concentrations were all varied. After injecting the TEOS, the product suspension was agitated for 24 h to complete the sol-precipitation of the silica in the reactor. Samples of the product suspension were then taken and completely dried at room temperature to analyze the hydroxyl group content of the silica particles using a thermal gravity analyzer (TGA: Shimadzu, DTG-60H, Japan). About 150 mg of silica particles was thermally scanned from 25 to 1250 °C at 5 °C/min in an argon flow, then the total hydroxyl group content in the silica particles was estimated from the weight loss. The specific surface area of the silica particles was also measured using the multipoint Brunauer–Emmett–Teller method (ASAP 2020, Micromeritis, U.S.A.).

3. Results and discussion

3.1. Thermal analysis of hydroxyl groups

The silica particles prepared using the Stöber method were spherically shaped. Although the silica particle size varied with the TEOS, water, and ammonia concentrations and reaction temperature, the particle size distribution remained highly mono-dispersed (within 2% of c.v.).

The typical thermogram and DTG curves for the silica particles are displayed in Fig. 1. Similar to the experimental results of Vansat et al. [9], two kinds of weight drop were observed for the silica particles during the course of the thermal scanning. The first rapid weight drop, occurring at 100–130 °C, was due to dehydration, meaning the removal of physisorbed water from the surface of the silica particles. The threshold temperature, corresponding to the completion of dehydration and the beginning of dehydroxylation due to the condensation of the OH groups in the silica particles, was then estimated as 190 ± 10 °C. Above this temperature, the silanes on silica particles were condensed to siloxanes, resulting in a significant weight drop for the silica particles across a broad temperature range from 200 up to about 600 °C. This second weight drop was due to the condensation of germinals and vicinals (Fig. 2 (b) and (c)), which were apt to convert to silica. However, the isolated silanols (Fig. 2(a)) were so stable that they were only slowly dehydroxylated at high temperatures above 600 °C, as previous reported by De Farias and Airoldi [5] and the Niinisto and coworkers [6].

Using attenuated total reflection spectrocsopy (FT-IR), the chemical bindings of the silica particles were scanned, as shown in Fig. 3. The typical absorption peaks for silica were found at 800 cm^{-1} for the symmetric stretching vibration ν_s(Si–O–Si), at 1098 cm^{-1} for the asymmetric stretching vibration ν_{as}(Si–O–Si), and at 464 cm^{-1} for the Si–O–Si bending mode.

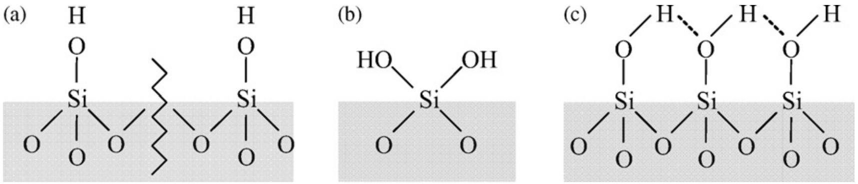

Fig. 2. Hydroxyl groups formed in silica particles prepared by sol-precipitation of TEOS: (a) isolated silanols, (b) germinals, and (c) vicinals.

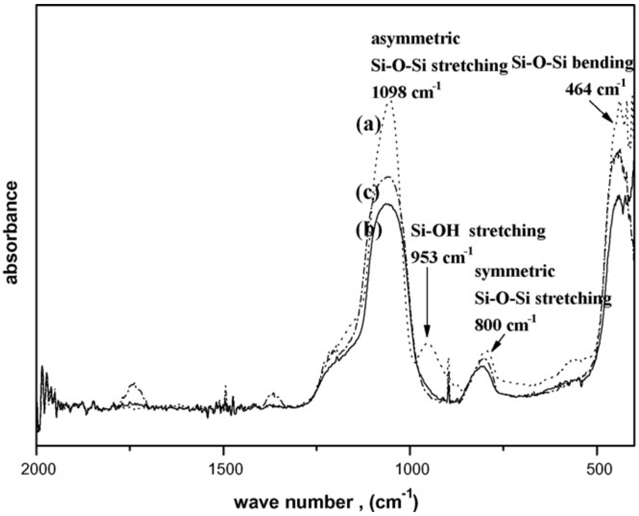

Fig. 3. ATR spectra of SiO_2 particles: (a) without calcination, (b) with calcination at 500 °C, and (c) with calcination at 900 °C.

In addition, the Si–OH stretching vibration was characterized at 953 cm^{-1} [14]. However, the characteristic peak intensity of Si–OH in the silica particles was reduced after calcination of the silica particles. After calcination at 500 °C, most of the vicinal and germinal hydroxyl groups were condensed, resulting in a significant decrease in the peak intensity of the Si–OH stretching in the silica particles. This peak of 953 cm^{-1} then completely disappeared after calcination at 900 °C, due to the dehydroxylation of the isolated silanols at a high temperature. It is interesting to note that the hydroxyl groups on the silica particles prepared by the sol-precipitation of TEOS were mostly composed of germinal and vicinals, and thus dehydroxylated at a low temperature of 600 °C, which was also supported by the thermogram (Fig. 1) of the silica particles.

3.2. Control of hydroxyl group content

When assuming that the condensation occurred based on the reaction of two types of hydroxyl group on the silica particles, the hydroxyl group content was estimated as follows, as previously suggested by Lauri Niinisto and coworkers [6]:

$$n_{\mathrm{OH}}(\mathrm{SiO_2}) = \frac{2(\mathrm{WL}(T_0) - \mathrm{WL}(T_{\mathrm{final}}))}{100 M_{\mathrm{H_2O}}} \tag{1}$$

$$\mathrm{OH}\,(\mathrm{nm}^{-2}) = \left(\frac{2(\mathrm{WL}(T_0) - \mathrm{WL}(T_{\mathrm{final}}))}{100 M_{\mathrm{H_2O}}}\right)\frac{N_{\mathrm{A}}}{S_{\mathrm{BET}}} \tag{2}$$

where $\mathrm{WL}(T_0)$ and $\mathrm{WL}(T_{\mathrm{final}})$ are the weight of the silica particles (wt%) at temperatures T_0 and T_{final}, respectively, $M_{\mathrm{H_2O}}$ is the molecular weight of the water, N_{A} is Avogadro's number, and S_{BET} is the specific surface area of the particles. Thus, in Eqs. (1) and (2), $n_{\mathrm{OH}}(\mathrm{SiO_2})$ and OH (nm^{-2}) indicate the moles of hydroxyl groups on the silica particles and the number of hydroxyl groups per unit area of the silica particles, respectively.

According to Raman spectroscopy, although carbon impurities resulting from the incomplete hydrolysis of TEOS were included in the silica particles, these were negligible in comparison with the second weight loss in the thermogram. Therefore, the hydroxyl group content on the silica particles prepared by the sol-precipitation of TEOS under various conditions could be effectively estimated from the thermogram (Fig. 1) using Eqs. (1) and (2).

In the sol-precipitation process, since the hydroxyl groups of silane are formed by the hydrolysis of TEOS and then condensed to silica consecutively [15], it would seem straightforward to assume that the hydroxyl group content on the silica particles is directly dictated by the reaction rates of the hydrolysis and condensation. Thus, when the sol-precipitation promotes hydrolysis more than condensation, this would increase the hydroxyl group content on the silica particles, and conversely the hydroxyl groups on the silica particles would be reduced when improving the condensation over the hydrolysis. As shown in Fig. 4, when increasing the ammonium concentration in the sol-precipitation, the hydroxyl group content increased from 5.7 to 42. 7 (OH/nm^2). In general, the nucleophilic substitution in the hydrolysis of TEOS is catalyzed by the OH^- in ammonia [16]. Meanwhile, the water condensation of the hydroxyl groups of silane was also improved by the ammonia. However, according to a previous kinetic study of sol-precipitation by Kim et al. [17], the catalytic effect of ammonia favored the hydrolysis of TEOS rather than the condensation of hydroxyl groups. In addition, the present study showed that, since the TEOS and water played direct roles in the hydrolysis as reactants, yet not in the condensation, the hydrolysis rate increased much more than the condensation when increasing the reactant concentrations. Consequently, the hydroxyl group content on the silica particles was increased when increasing the TEOS and water concentrations (Figs. 4(b) and (c)). According to Yoon et al. [18], increasing the temperature increases both hydrolysis and condensation. However, since the activation energy of condensation is higher than that of hydrolysis, an incremental increase in the reaction temperature facilitated condensation more than hydrolysis, resulting in a reduction of the hydroxyl group content from 34.1 to 10.2 (#/nm^2) on the silica particles

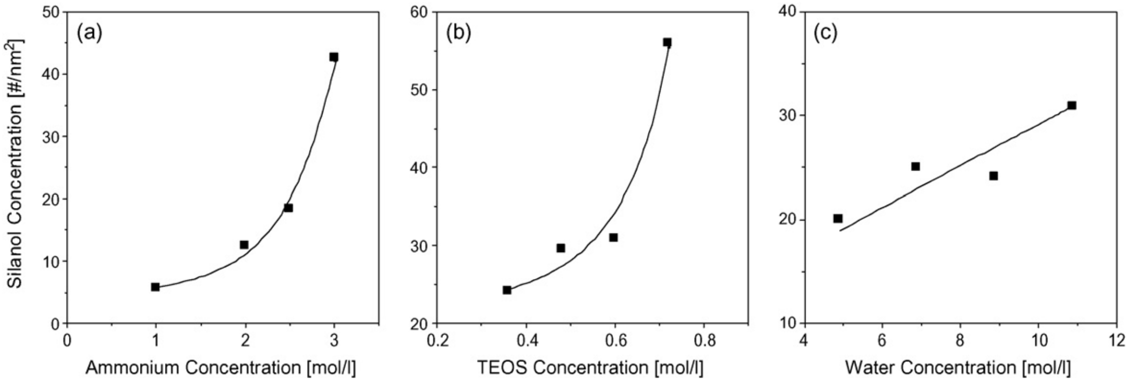

Fig. 4. Variation of hydroxyl group concentration in silica particles relative to reaction conditions: (a) ammonium concentration, (b) TEOS concentration, and (c) water concentration. The other reaction conditions were fixed, as summarized in Table 1.

Table 1
Analysis of hydroxyl group content in silica particles using TGA

Reaction condition				Mean diameter (nm)	Surface area (m^2/g)	Second mass loss at 1100 °C (%) (after neglecting impurity weight loss)	*M* (mg)	OH group content (mmol/g)	Silanol number (OH/nm^2)
TEOS (mol/l)	NH_3 (mol/l)	H_2O (mol/l)	Temperature (°C)						
0.6	1	7.28	25	247	22.4	0.19	164.06	0.211	5.7
0.6	2	7.28	25	527	6.94	0.13	173.25	0.144	12.5
0.6	2.5	7.28	25	570	7.63	0.21	169.91	0.233	18.4
0.6	3	7.28	25	613	5	0.32	175.99	0.355	42.7
0.6	2	4.88	25	581	4.76	0.22	152.64	0.244	20
0.6	2	6.88	25	474	6.96	0.2	163.77	0.222	25.1
0.6	2	8.88	25	494	6.92	0.26	175.62	0.289	24.1
0.6	2	10.88	25	457	7.36	0.22	163.32	0.244	30.9
0.36	2	10.88	25	349	21.05	0.76	153.05	0.844	24.1
0.48	2	10.88	25	438	5.42	0.24	152.73	0.266	29.6
0.6	2	10.88	25	581	4.76	0.22	152.64	0.244	30.9
0.72	2	10.88	25	501	4.06	0.34	160.87	0.377	56
0.6	2.5	10.88	25	551	3.35	0.39	175.69	0.433	34.1
0.6	2.5	10.88	40	184	24.84	0.38	167.42	0.422	10.2

when changing the temperature from 25 to 40 °C, as summarized in Table 1.

4. Conclusions

A TGA thermogram was used to make an effective quantitative estimation of the hydroxyl group content in silica particles produced by sol-precipitation. In a thermal scan of silica particles, dehydration occurred below 190 °C, followed by dehydroxylation above 200 °C. Most of the hydroxyl group weight loss was due to the dehydroxylation of germinals and vicinals between 200 and 600 °C, while the isolated silanols only disappeared at above 600 °C. The dehydroxylation of the silanes on the silica particles relative to temperature was confirmed using FT-IR.

Since silanes as intermediates are formed by the hydrolysis of TEOS and then converted to silica during the process of sol-precipitation, the hydroxyl group content in the resulting silica particles is directly dictated by the relative rates of hydrolysis and condensation, which was shown to depend on the reaction conditions, specifically the TEOS, water, and ammonia concentrations and reaction temperature. When the hydrolysis of TEOS was promoted more than the condensation of the hydroxyl groups, as when increasing the ammonia, TEOS, and water concentrations, this increased the hydroxyl group content on the silica particles. Meanwhile, the hydroxyl group content was reduced when increasing the temperature due to its promotion of condensation.

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