Influences of pretreatment temperature on the surface silylation of diatomaceous amorphous silica with trimethylchlorosilane

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Abstract

Diatomaceous amorphous silica samples were modified by silylation using trimethylchlorosilane (TMCS). The resultant materials were characterized by using thermogravimetry (TG), ^{1}H magic-angle spinning nuclear magnetic resonance (^{1}H MAS NMR), Fourier transform infrared spectroscopy (FTIR) and chemical analysis. The degree of silylation was found to increase with the increasing temperature of thermal pretreatment on diatomaceous silica prior to silylation. Increment of the pretreated temperature leads to stepwise removal of physisorbed water followed by the dehydration of capping water that H-bonded with the surface silanols, resulting in exposure of more and more isolated and H-bonded silanols previously covered by water molecules. Among these exposed silanols, isolated silanols show high activity for silylation reaction but H-bonded ones show poor activity. The maximum degree of surface attachment of TMCS grafted onto the diatomaceous silica (about 1.81 mmol TMCS groups per gram of silica) was shown in the sample pretreated at 1100 °C, in which the amount of exposed isolated silanols get the maximum. The fundamental information derived from this work is of significance in well understanding the surface silylation reaction of diatomaceous silica and providing useful information for related industrial production.
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1. Introduction

Diatomite, also known as diatomaceous earth or kieselgur, is classified as a siliceous sedimentary rock resulting from the accumulation and compaction of fossilized remains of diatoms over geological time scales. The primary inorganic component of diatom shell has been found to be a sort of biogenic amorphous silica that has many useful properties (e.g. high porosity with strong adsorbability, low density, low thermal conductivity, high melting point and chemical inertness). Consequently, diatomite has been used in a variety of applications, including uses as filter, abrasive, catalytic support, cosmetic, filler, and absorbent [1].

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As is well known, the silica surface consists of siloxane bridges and different types of hydroxyl groups (i.e. silanols), which are key reactive sites for various surface reactions: wetting, dispersion in solutions, adsorption, and surface modification (e.g. silylation) etc. [2,3]. The distribution and evolution of different types of silanols and siloxanes largely depend on thermal treatment condition, as well as on ambient humidity and storage time [4]. Many studies have been developed to investigate the properties of silanols on the surface of some synthetic silicas by various characterization methods, including chemical reaction [5,6], adsorption [7], and spectroscopic method (IR [8,9], NMR [4,10–13], etc.). Much attention was also paid to the surface modification of synthetic silica [14–18].

However, compared to the numerous studies focused on synthetic silicas and some biogenic silica from plants (leaves and rice husk, etc.) [19,20], much less attention was paid to the naturally yielded diatomaceous silica as an abundant mineral resource.

Bertermann et al. investigated the degree of condensation of silanols (i.e. the reaction by $2 \equiv SiOH \rightarrow \equiv Si–O–Si\equiv + H_2O$) of four different living diatom species by quantitative ^{29}Si MAS NMR experiments [21]. Their results revealed that there seemed to be no obvious differences regarding the silica architecture among different diatom species. However, Gendron-Badou et al. demonstrated a dramatic difference between fossil diatom shells (abstracted from diatomite) and living diatoms. The former exhibited a highly condensed structure containing relative small amount of silanols whereas the latter is much less condensed but contains more abundant silanols [22].

On the other hand, a few studies focused on surface modification of fossilified diatomaceous amorphous silica (hereafter abbreviated as diatom-silica) have been developed to extend the applications of diatomite. Huttenloch et al. modified the diatomite surface from polar to lipophilic by use of chlorosilanes. As a result, the sorption of some nonpolar aromatic contaminants onto the modified diatomite showed a great enhancement compared to that of the untreated diatomite [23]. The modified diatomite was thereby thought as an effective sorbent for removing organic contaminants from wastewater [23]. In another work, diatomite modified with polyaniline exhibited some potential commercial applications as functional fillers for electromagnetic shielding materials and conductive coatings [24].

Generally, previous studies paid great attention to the actual modification effect rather than the mechanism of surface modification reaction, and a well understanding on the surface properties of diatom-silica has not yet been achieved. Due to the surface properties of diatom-silica differ from those of synthetic amorphous silicas in some ways, as indicated by our previous reports [25,26], the related results derived from previous studies on synthetic amorphous silicas should not be simply transplanted to the diatom-silica. Consequently, further work focused on the surface properties, as well as the mechanism of interface reaction of diatom-silica is worthwhile.

Our previous reports showed that the increase of thermal pretreatment temperature has a prominent effect on the types, distribution, and content of surface hydrated species (water, H-bonded silanols, and isolated silanols) [25–27]. Thus, an interesting question arises, i.e., if and/or how the pretreatment temperature influences the surface modification reaction of diatom-silica in mechanism and efficiency? To answer this question, in this work, a series of thermally pretreated diatom-silicas were modified by silylation with trimethylchlorosilane (TMCS), and the influences of the pretreatment temperature on the silylation reaction were investigated by using thermogravimetry analysis (TG), ^1H magic-angle spinning nuclear magnetic resonance (^1H MAS NMR), and Fourier transform spectroscopy (FTIR). The obtained results are of importance in understanding the modification reaction mechanism between diatom-silica and silane, as well as in providing some useful information for related industrial production of diatomite.

2. Experimental

2.1. Materials and silylation reaction

Raw diatomite sample was collected from Buchang deposit in Haikang county of Guangdong province, China. Micromorphology observation by SEM showed that most of diatoms in Buchang diatomite sample belong to the genera *Synedra ulna* (Nitz.) Ehr. [26]. Purification of the raw sample included repeating sedimentation processes followed by four times of acid-washing process, of which a 2 M HCl solution was used and the mixture was kept at 105 °C for 4 h, with a ratio of HCl solution: diatomite = 15 cm^3: 1 g of diatomite. At the end of each acid-washing process, the diatomite suspension was centrifuged and washed repetitiously until free of Cl$^-$ (tested by AgNO$_3$). The purified diatom-silica (hereafter denoted as PD) was dried at 105 °C for 24 h, ground into powder in mortar, and then kept in a desiccator. One purpose of using a combination of acid-washing and sedimentation for purification, rather than a single sedimentation method used in our previous work [26,27], is to remove the fine impurities (e.g. ferreous minerals) that are hard to be eliminated only by sedimentation. Another purpose is to let the experimental condition be closer to an actual industrial purification in which acid-washing method is generally applied.

Thermal pretreatment was performed by heating diatom-silica samples in muffle oven at 200, 400, 600, 800, 1000, and 1100 °C for 1 h. The corresponding weight loss (relative to PD) of these pretreated samples, WL (wt.%), measured by an analytical balance, are 4.12%, 4.88%, 6.04%, 6.94%, 7.14%, and 7.24% (Table 1), respectively. Part of each resulting sample was enveloped in a polyethylene sample bag and placed in ambient condition (the room temperature was ca. 27 ± 2 °C, and the relative humidity is about 70 ± 5%) for 30 days, to evaluate the rehydration behavior of these pretreated diatom-silica samples in a

Table 1
Content of loaded TMCS and some weight losses obtained from chemical and thermal analysis

Properties	Related pretreatment temperature (°C)						
	[a] RT	200	400	600	800	1000	1100
[b] WL (%)	0	4.12	4.88	6.04	6.94	7.14	7.24
[c] W (%)	1.37 ± 0.08	1.93 ± 0.02	2.29 ± 0.17	2.58 ± 0.07	4.02 ± 0.18	8.12 ± 0.18	13.21 ± 0.16
[d] M (mmol/g)	0.19 ± 0.01	0.26 ± 0.01	0.31 ± 0.02	0.35 ± 0.01	0.55 ± 0.02	1.11 ± 0.03	1.81 ± 0.02
Loss-W (%)	7.35 ± 0.02	6.11 ± 0.02	5.13 ± 0.01	2.40 ± 0.02	≈0	≈0	≈0
Loss-S (%)	2.81 ± 0.03	2.20 ± 0.03	0.91 ± 0.02	≈0	≈0	≈0	≈0
Loss-T (%)	≈0	≈0	≈0	1.82 ± 0.03	2.40 ± 0.01	7.84 ± 0.02	13.63 ± 0.01
[e] Total loss	10.16 ± 0.01	8.31 ± 0.01	6.04 ± 0.01	4.22 ± 0.01	2.40 ± 0.01	7.84 ± 0.02	13.63 ± 0.01

[a] Room temperature, corresponding to samples PD and PD-T.
[b] WL, the weight loss (relative to PD) of these pretreated diatom-silica samples.
[c] W and [d] M, the content of loaded TMCS in silylated diatom-silica.
[e] Total Loss = Loss-W + Loss-S + Loss-T.

not very strict storage condition which is close to an industrial storage condition. The rest of samples were kept in a desiccator for silylation and characterization.

Surface silylation reactions were carried out by exposing pretreated diatom-silica samples to saturated vapors from refluxing TMCS reagent for a period of 6 h. The reaction temperature was maintained at 80 °C. The silylated samples were further evacuated at 105 °C to remove the physically adsorbed TMCS molecules.

The final thermally pretreated samples, rehydrated ones, and silylated ones are differentiated on the basis of pretreatment temperature. For instance, the diatom-silica sample thermally treated at 200 °C is referred as PD-200, and the derivatively rehydrated and silylated one are denoted as PD-200-R and PD-200-T, respectively.

2.2. Characterization

The chemical composition of PD was determined using a PE-3100 atomic absorption spectrometer (AAS). The content of the loaded TMCS, W (wt.%), in silylated diatom-silica samples was calculated from the carbon content, which was obtained by averaging two measurement results recorded by a Vario El III elementar analyzer. The corresponding value of molar density, M (mmol/g), was obtained by the equation of $M = 1000 \times W/EMW$, and the number of TMCS groups, N (number/nm^2), was calculated by $N = W \times A/EMW \times S_{BET} \times 10^{18}$, where A is Avogadro's constant (6.02×10^{23}), EMW is the effective molar weight of the grafted TMCS (73.1 m^2/g), and S_{BET} (m^2/g) is the specific surface area.

A Rigaku D/max-1200 X-ray diffractometer (CuKα radiation under target voltage of 40 kV and current of 30 mA, $\lambda = 0.154$ nm) equipped with a graphite monochromator was used to acquire the XRD patterns of the powdered samples. S_{BET} was measured by the BET method at liquid nitrogen temperature with a gas sorption analyzer (Quantachrome, NOVA 1000). Prior to measurement, the sample was outgassed at 250 °C at a pressure less than 10^{-3} Torr for 3 h.

Thermogravimetry analysis (TG) was performed on a Netzsch STA 449C instruments. 10 ± 0.1 mg of finely ground sample was heated in an open corundum crucible. The heating range was from 50 to 1150 °C at a heating rate of 10 °C/min under highly pure nitrogen atmosphere.

The MAS-NMR one-pulse spectra of ^{1}H were recorded on a Varian Infinityplus-400 spectrometer at Larmor frequency of 400.12 MHz. The powdered samples were packed in 5 mm (outer diameter) zirconia rotor with polytetrafluoroethylene (PTTE) endcaps and the speed was 4 kHz. A 4.9 μs excitation pulse with 90° flip angle and 6 s recycle delay was used, and the transients were 600 times. The chemical shift of proton was determined by tetramethysilane (TMS) as external reference.

The FTIR spectra of the samples were recorded on a Nicolet 470 FTIR spectrometer. Specimens for measurement were prepared by mixing 0.9 ± 0.01 mg of the sample powder with 70 ± 0.1 mg of KBr and pressing the mixture into a pellet. The average over 32 scans was collected for each measurement in a wavenumber range of 2500–4000 cm^{-1} with a resolution of 0.5 cm^{-1}.

3. Results and discussion

3.1. Characterization on purified diatom-silica

The PD was shown to have a chemical composition (wt.%) as SiO$_2$, 90.12; Fe$_2$O$_3$, 0.32; CaO, 0.47; MgO, 0.17; TiO$_2$, 0.40; loss, 7.94, and its specific surface area is 56.3 ± 1.1 m^2/g. The XRD pattern of PD (Fig. 1(a), the insert) is characteristic of one very broad peak centered at ca. 21.8° (2θ) ($d = 4.09$ Å), indicating that this sample is primarily composed of amorphous silica.

In the DTG curve of PD (Fig. 1(a)), the peaks at ca. 110 and 155 °C should be assigned to the desorption of physisorbed water from the surface of diatom-silica, consistent with the proposed desorption temperature (100–180 °C) of physisorbed water of silica samples (Aerosil, MCM-41, Kieselgel, etc.) [2,28]. However, the temperature at which most physisorbed water is dehydrated might be at ca. 260 °C as shown by the TG curve, a bit higher than that at ca. 200 °C reported by Zhuravlev [29,30]. In the DTG curve of PD, another broad and poor-resolved peak centered at ca. 700 °C should be ascribed to the dehydroxylation of
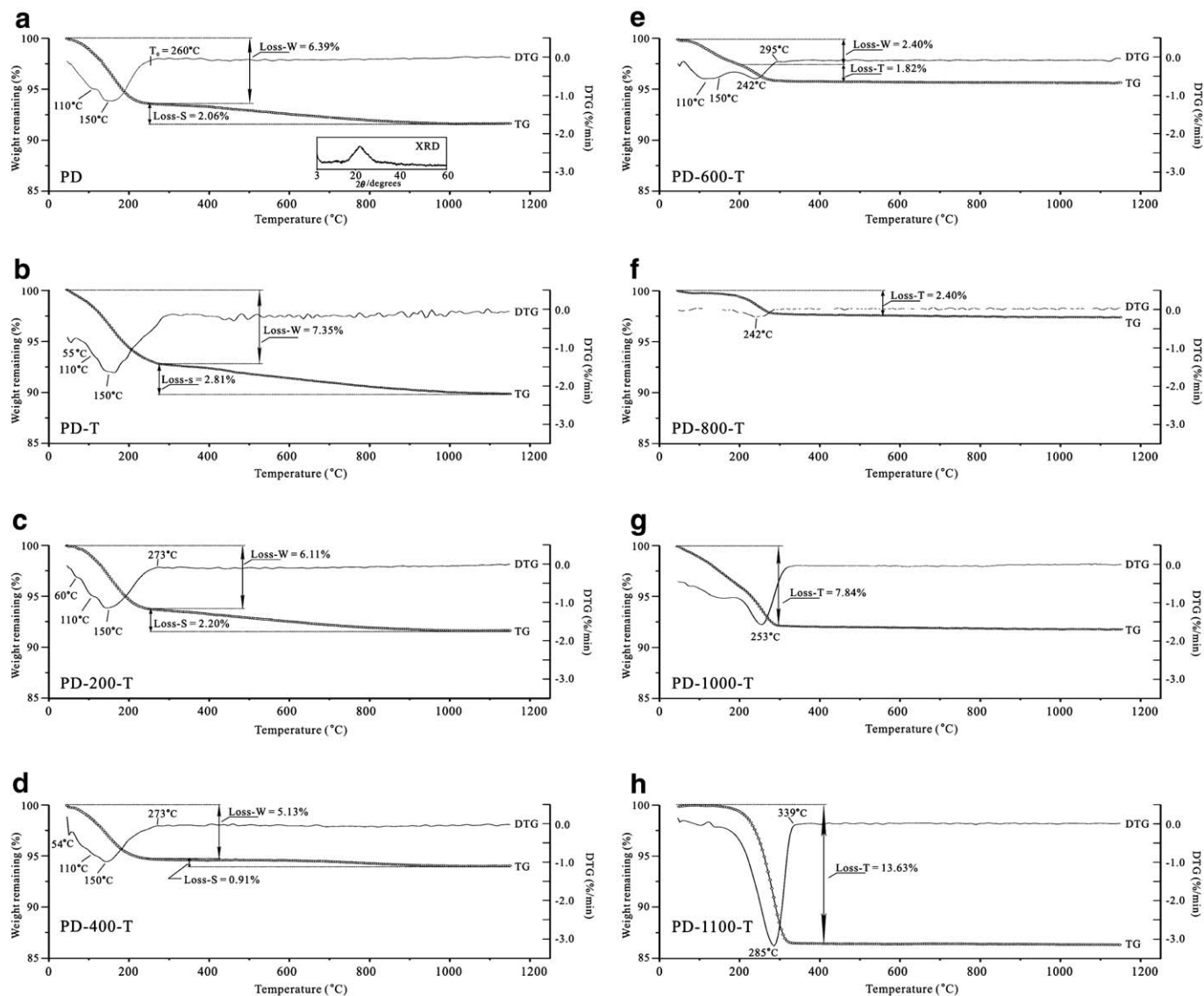
Fig. 1. TG and DTG curves of diatom-silica samples.

silanols. This assignment is well supported by the second weight loss step shown in the TG curve.

TG was proposed as a simple method to measure the content of silanols and physisorbed water of silica [2]. This method is based on the assumption that the dehydration and dehydroxylation reactions correspond to the two discrete weight loss steps in TG curve and they do not overlap each other [2]. Consequently, the physisorbed water content can be directly calculated from the first weight loss $W(T_0)$ (hereafter noted as Loss-W, as shown in Fig. 1), where T_0 is the temperature at which all of the physisorbed water is dehydrated and silanols start to condense. And the density of silanols (n_{OH}, mol/g) can be calculated by $n_{OH} = 2[W(T_{end}) - W(T_0)]/M_{H_2O}$, where T_{end} is the endpoint of temperature (1150 °C), $W(T_{end})$ is the total weight loss (wt.%), and M_{H_2O} is the molar mass of water. The value of $W(T_{end}) - W(T_0)$ is noted as Loss-S (shown in Fig. 1(a)).

By above-mentioned calculation on the basis of the values of Loss-W (6.39 ± 0.02%) and Loss-S (2.06 ± 0.03%) indicated by the TG curve of PD in Fig. 1(a), ca. 3.55 mmol/g (corresponding to 38.0 H_2O/nm^2) for the density of water and ca. 2.29 mmol/g (24.5 OH/nm^2) of silanols are obtained. This high-density value of water indicates that there must exist multilayer rather than monolayer water molecules adsorbed on the surface. However, the density of silanols (24.5 OH/nm^2) seems to be overestimated, compared with the reported value of only 4.0–8.5 OH/nm^2 observed on over 100 different silica samples with different origin and structural characteristics [13,29].

One possible reason results in this overestimate might be due to the underestimate on S_{BET} of PD. Humbert reported that underestimate of surface area usually occurs and thus yields a much overestimated value of silanols density derived from TG, when a materials contains micropores

or very small channel which water molecules can enter (by H-bond) but nitrogen cannot [13]. This case is applicable for the diatom-silica owing to its hierarchically porous structure as reported in the literature [31].

On the other hand, our previous report has demonstrated that in diatom-silica some water molecules which H-bonded with silanols cannot be dehydrated until 600 °C [26]. Hence, the value of Loss-W corresponds to dehydration of partial water rather than all adsorbed water. The value of Loss-S is therefore exaggerated, yielding an overestimated value of the silanols content. This result indicates the assumption that dehydration and dehydroxylation steps do not overlap might be not reasonable for diatom-silica and directly result in the overestimate on the density of silanols. Similar result that (de)hydration actually overlapping with (de)hydroxylation was also observed in some synthetic amorphous silicas [32].

In avoiding the effects of water molecules during determining the content of silanols, Solid-state ^{29}Si NMR spectroscopy might be more advantageous than TG method, since it directly detects the signals of silanols associated with the Si atoms (see report by Legrand et al. for detail [12]). Thus the adsorbed water does not interfere with these signals [12,13]. However, Humbert found that the ^{29}Si NMR method also tends to yield an overestimated density of silanols, when there exists a type of Q^4 silicon atom contained in a $(SiO)_3$-ring in the tested amorphous silica [13,33]. In this case, Humbert demonstrated that a comprehensive characterization of ^{29}Si NMR and Raman spectroscopy is necessary to obtain a reasonable result of the content of silanols [13]. Our previous work has revealed that there did exist $(SiO)_3$-ring structure in diatom-silica [25], suggesting that the determination on density of silanols is complicate due to a combined analyses of NMR and Raman is necessary. Our related work is underway.

3.2. Chemical and thermal analysis of silylated diatom-silica

Fig. 1(b)–(h) is the TG and DTG curves of the modified diatom-silica samples. In the DTG curves, the peaks centered at ca. 110 ± 1 and 150 ± 1 °C exhibited in PD-T,

PD-200-T, PD-400-T, and PD-600-T (Fig. 1(b)–(e)) are attributed to the dehydration of water molecules, corresponding to the Loss-W in the corresponding TG curves. On the other hand, the very broad DTG peak centered ca. 700 ± 5 °C is related to the long-term dehydroxylation process, which is indicated by the values of Loss-S in the TG curves. These results are analogous to that of PD, indicating that the grafting of TMCS is not obvious in these samples. It is noteworthy that the total weight loss of PD-T ($10.16 \pm 0.01\%$) is shown to be even higher than that of PD ($8.45 \pm 0.01\%$). This result is due to the addition of weight losses not only from physisorbed TMCS whose DTG peak is at 55 ± 5 °C (Fig. 1(b)–(e)) but from partial grafted TMCS whose peaks might be overlapped by the peaks of water or silanols.

At the pretreatment temperature of 600 °C (Fig. 1(e)), a new DTG peak centered at ca. 242 ± 1 °C appears. It should be ascribed to the decomposition of the silylated TMCS, indicating the formation of much stronger bond between TMCS and the surface of pretreated diatom-silica. Regarding this peak, a weight loss (hereafter noted as Loss-T) of the silylated TMCS can be resolved in the TG curve, and the Loss-T should be taken as an indicator of the content of the grafted TMCS.

In the cases of PD-800-T, PD-1000-T and PD-1100-T (Fig. 1(f)–(h)), the DTG peak corresponding to grafted TMCS becomes dominant, reflecting that silylation is obviously achieved. And the best silylation occurs in PD-1100-T due to its highest weight loss (ca. $13.63 \pm 0.01\%$) corresponding to the strongest DTG peak centered at 285 ± 2 °C. Accordingly, pretreatment at 1100 °C for 1 h seems to be the most favorable condition in this work for the silylation of diatom-silica by TMCS. It can be seen that this result is well consistent with the chemical analysis result shown in Table 1.

Fig. 2 represents the relationship among the pretreatment temperatures, the content of grafted TMCS, and the different weight losses (presented in Table 1). Fig. 2(a) indicates that the increase of pretreatment temperature results in a stepwise increment in the content of TMCS. Fig. 2(b) demonstrates that the WL value, which
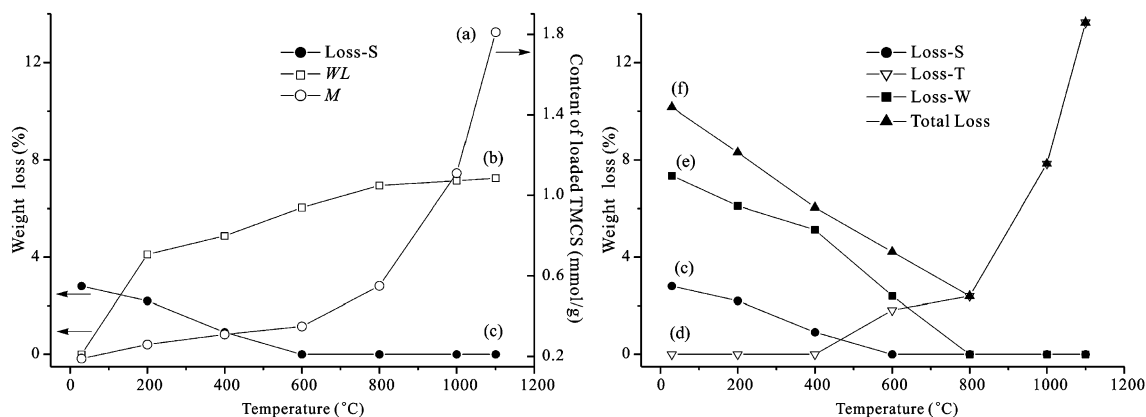

Fig. 2. The relationship among pretreatment temperatures, the content of grafted TMCS, and different weight losses.

is negatively related to the content of water molecules remained in pretreated sample, increases with the increase of the pretreatment temperature. Consequently, it can be deduced that the removal of water in advance is favorable for the silylation.

On the other hand, due to that the Loss-S reflects the approximate content of silanols contained in the pretreated samples, Fig. 2(a) and (c) shows that the silanol content decreases with the increase of temperature, indicating that the silylation leads to the consumption of silanols.

Fig. 2(d)–(f) shows that the weight loss is almost entirely derived from the loaded TMCS for the samples pretreated above 800 °C, in which water is completely removed. This result also indicates that removal of water is helpful for the silylation.

According to above thermal analysis results, an understanding can be deduced that a high pretreatment temperature is favorable for silylation, and the silanols should be the reactive sites for the silylation. Nevertheless, how the types and distribution of hydroxyl species (water and different types of silanols) affect the silylation is not clear yet, so spectroscopic analysis is applied to answer this question.

3.3. ^1H MAS NMR and FTIR analysis

^1H MAS NMR spectra of diatom-silicas (before silylation) are shown in Fig. 3. Five proton peaks are resolved by Gauss deconvolution and their resonances are 2.1 ± 0.1, 3.5 ± 0.1, 4.8 ± 0.1, $6.1–7.1 \pm 0.1$, and 0.5 ± 0.1 ppm, respectively (Fig. 3). The peaks at 2.1, 4.8, and 6.1–7.1 ppm should be attributed to the protons of isolated silanols, physisorbed water, and H-bonded silanols, respectively. This assignment is well in accordance with the ^1H MAS NMR spectra of synthetic amorphous silicas [11] and our previous report [27]. However, to the best of our knowledge, the proton signal at ca. 0.5 ppm has not been mentioned in the literature.

Considering the diatom-silica samples used in this work underwent leaching with a high concentration of HCl, unlike those in our previous work were purified only by sedimentation method, the peak at 0.5 ppm might be considered as resulting from some special isolated silanols (e.g., from the $\equiv Si–OH_2^+$). These silanols are the products of the reaction between surface isolated silanol ($\equiv Si–OH$) and H^+ in an acidic aqueous solution with a high concentration of HCl [34]. In this case, the $^1H–^1H$ dipole–dipole interactions between the two protons will lead to a line-broadening of the related signal. As shown in Fig. 3(a), a broad signal center at 0.5 ppm is recorded, providing an evidence for the above-mentioned assignment.

The peak at ca. 3.5 ppm was attributed to the protons of water that H-bonded to silanols in our previous report, based on its evolution behavior under dehydration condition [27]. However, d'Espinose de la Caillerie et al. ascribed this peak to the silanols H-bonded to water in investigating
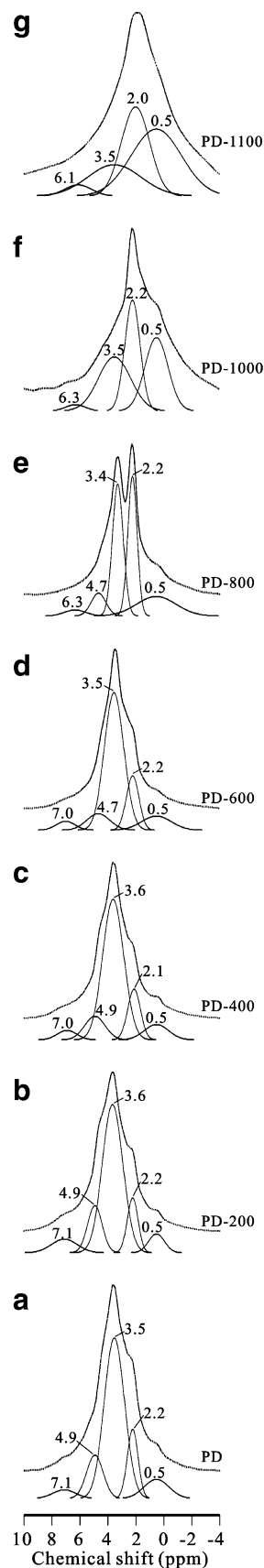

Fig. 3. ^1H MAS NMR spectra of diatom-silica samples (before silylation).

the synthetic amorphous silica Cabot Cab-O-Sil H5 and Aerosil A200 [32]. In consideration of the strong similarity [11] of the chemical and physical environments of protons respectively from H-bonded silanols and their associated H-bonded water (so called 'capping' water [32]) molecules, it would not be surprising for the overlapping of the signals of these two types of protons. In another words, the peak at 3.5 ppm should be attributed to the protons between the interface of silanols and capping water molecules.

Presented in Table 2 are the relative contents of each proton species in diatom-silica samples (before silylation), which are expressed as the percentage (%) of integral area for different ^{1}H MAS NMR peaks. It can be seen that an increase of the pretreatment temperature will lead to the removal of water, as well as yield more silanols. This is well consistent with the TG result. Here, it can be found that the ^{1}H MAS NMR is more informative than TG in determining capping water, physisorbed water and different types of silanols.

Based on above assignments, the types of different proton species in diatom-silica and their behavior under thermal treatment are schematically illustrated in Fig. 4. Without thermal pretreatment, most of isolated silanols and H-bonded ones are H-bonded with capping water molecules. There exist physisorbed water molecules on the

ground of the layer of capping water (Fig. 4(a)). The physisorbed water is movable with liquid-like structure, since its chemical shift is very close to that of liquid water (at ca. 5.0 ppm).

Thermal pretreatment will lead to the dehydration of the physisorbed water followed by dehydration of capping water, resulting in exposure of more silanols (Fig. 4, schemes *I* and *II*). However, decrease in the amount of capping water and physisorbed water is not obvious at temperature lower than 600 °C, as shown in Table 2, and a dramatic decrease happens in the temperature range of 800–1100 °C. At 1100 °C, water molecules have been removed and the content of silanols gets the maximum.

In the ^{1}H MAS NMR spectra of silylated samples, two new signals (at 1.5 and 1.2 ppm respectively) are recorded (Fig. 5(A)). The signal at 1.5 ppm should be attributed to the TMCS grafted onto the isolated silanols (at ca. 2.1 ppm), and the one at 1.2 ppm to the TMCS grafted onto the special isolated silanols (at ca. 0.5 ppm). This result reflects the two types of protons, respectively from grafted TMCS onto the two types of isolated silanols, has some minor differences in chemical environment. As shown in Fig. 5(A), the degree of silylation, which corresponds to the signal intensity of grafted TMCS, is positively related to the pretreatment temperature. Meanwhile, the signal

Table 2
Percentage of the peak area of each deconvoluted peak in the ^{1}H MAS NMR spectra of diatom-silica samples

| Samples	Percentage (%) of the integral area of each proton species, characteristic of different ^{1}H chemical shifts					R^2	Fit standard error
	0.5 ± 0.1 ppm	2.1 ± 0.1 ppm	$6.1–7.1 \pm 0.1$ ppm	3.5 ± 0.1 ppm	4.8 ± 0.1 ppm		
PD	9.0	13.7	3.8	60.0	13.5	0.971	3.75
PD-200	6.0	11.8	7.1	61.2	13.9	0.987	2.76
PD-400	8.1	13.9	4.0	63.5	10.5	0.988	2.54
PD-600	9.8	15.7	3.9	61.5	9.0	0.985	2.98
PD-800	19.5	32.7	3.3	35.8	8.6	0.926	6.28
PD-1000	32.4	32.0	2.3	33.2	0.0	0.957	4.49
PD-1100	36.9	39.0	5.5	18.7	0.0	0.983	3.39
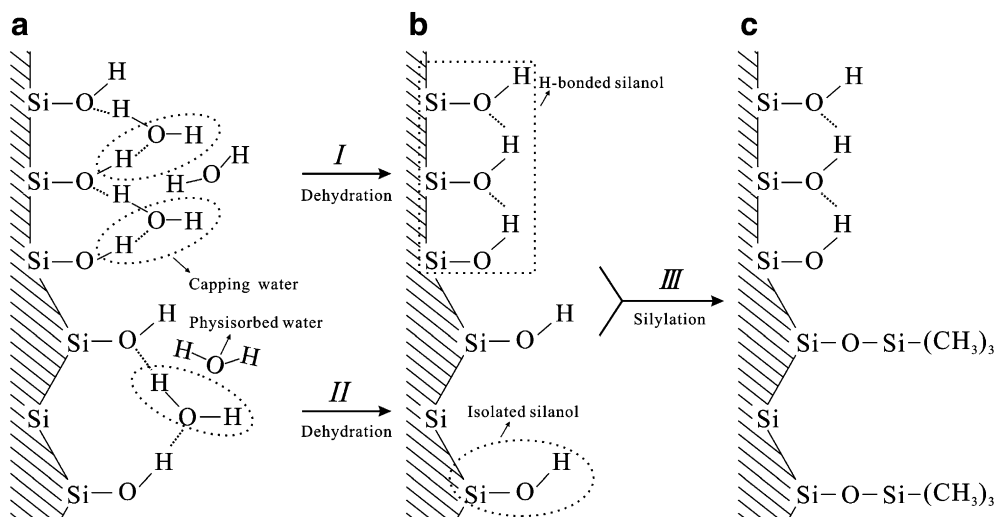
Fig. 4. A schematic representation of the types of proton species on diatom-silica surface and their roles in silylation reaction.
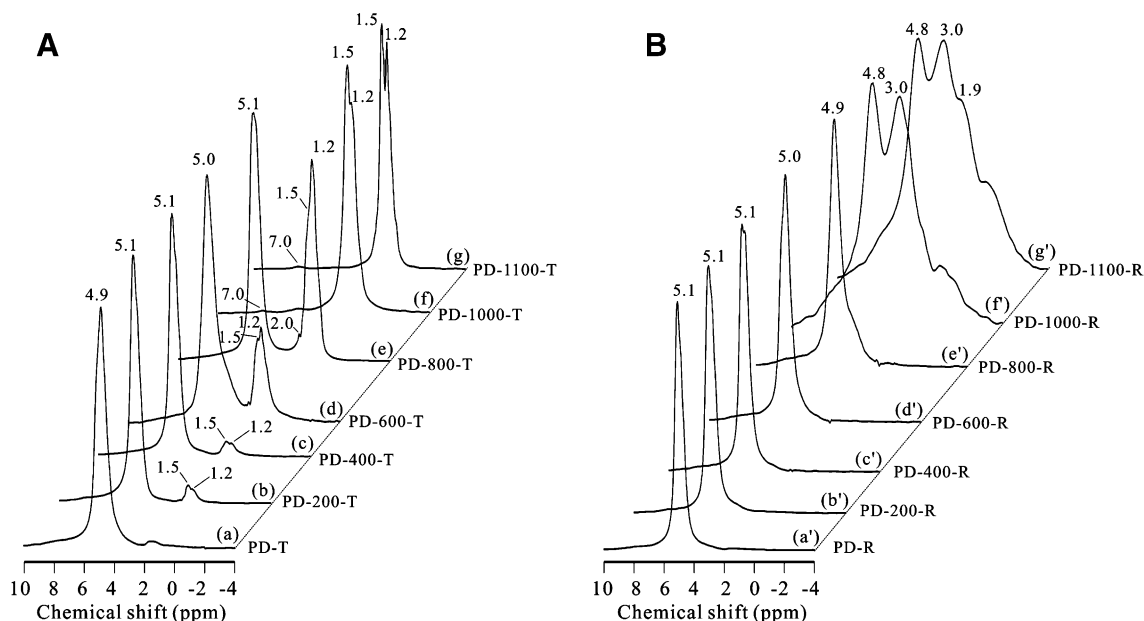
Fig. 5. ^{1}H MAS NMR spectra of (A) silylated diatom-silica samples and (B) rehydrated diatom-silica samples.

intensity of isolated silanols is dramatically reduced. This indicates that the silylation reaction is based on the consumption of isolated silanols, i.e. the grafting reaction of $\equiv$Si–OH + Cl–Si–(CH$_3$)$_3$ → $\equiv$Si–O–Si–(CH$_3$)$_3$ + HCl happens between isolated silanols and TMCS, as shown in Fig. 4 (scheme III). In contrast with that, the peak of H-bonded silanols (at ca. 7.0 ppm) is still exhibited in the spectrum of PD-1100-T, suggesting that the H-bonded silanols is poorly reactive for the silylation. The activity of isolated silanols and the poor activity of H-bonded ones for silylation by TMCS were also found in the cases of some synthetic silica (e.g., MCM-41 [35,36] and Grace SD 3216.20 [16]).

The existence of capping water is unfavorable for the silylation, since they cover on silanols to prevent them from reacting with TMCS. On the other hand, capping water plays a key role as favorable 'ground' for the physically adsorption of water molecules. As a result, rehydration easily happens even in the silylated samples, as indicated by the existence of the peak of physisorbed water (at ca. 5.0 ppm) (Fig. 5(a)–(e)). For PD-1000-T and PD-1100-T, capping water is mostly removed and thus exposed silanols are grafted with hydrophobic TMCS, resulting in no rehydration observed in these cases(Fig. 5(f) and (g)).

Here, it can be seen that sufficient exposure of isolated silanols is essential for the silylation. The exposure extent of silanols strongly depends on the removal of physisorbed water and the dehydration of capping water, which increases with an increase of the pretreatment temperature. This dependency can well explain the results of chemical and thermal analyses. This study suggests that a favourable condition for silylation starts at the temperature of the completely dehydration of water and the best silylation

occurs at the temperature where isolated silanols have the highest content.

Shown in Fig. 6 are the FTIR spectra of silylated diatom-silica samples. The peaks at 2852 ± 1, 2920 ± 1, 2963 ± 1 cm^{-1} are attributed to the vibration modes of the grafted TMCS [16,35,37]. The intensities of these bands increase with the increment of pretreatment temperature, and get the maximum at 1100 °C. Meanwhile, the band of isolated silanols (at ca. 3745 cm^{-1}) [17,26] is not shown in the spectra, indicating that all of the isolated silonals are consumed in the silylation reaction. However, the OH
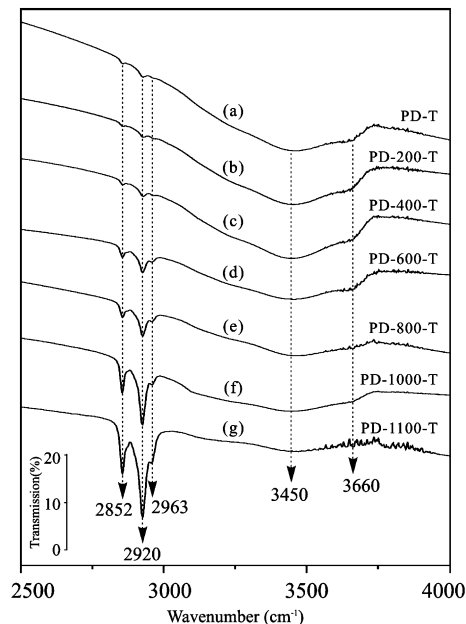

Fig. 6. FTIR spectra of silylated diatom-silica samples.

vibration mode (at ca. 3660 cm^{-1}) of H-bond silanols [38] can still be resolved in the spectra, suggesting that the H-bond silanols are poorly reactive for silylation. Consequently, the IR result provides an extra support to the results obtained from chemical, thermal, and ^{1}H MAS NMR.

3.4. Evaluation on the silylation of diatom-silica

The content of loaded TMCS in PD-1100-T (1.81 ± 0.02 mmol/g) is close to that of TMCS loaded in MCM41, reported by Wounters et al. (ca. 1.1 mmol/g) [36] and Zhao et al. (ca. 1.99 mmol/g) [37]. However, the number of TMCS groups, N (number/nm^2), is ca. 19.3/nm^2 based on the value of S_{BET}. This value is unreasonably high considering the steric hindrance of grafted TMCS groups, indicating that the S_{BET} is actually underestimated as above discussed. Relative to the silanols density (2.29 mmol/g), a high coverage of TMCS on silanols (about 79.0%) is obtained. This high degree of silylation might be not so surprising, since all of the surface silanols of diatom-silica are shown to be accessible to water as well as TMCS. This property is analogous to that of precipitated silica (e.g. silica gel) but not to some pyrogenic silicas (e.g. Cabot Cab-O-Sil H5 and Aerosil A200). In the latter case, there are considerable internal silanols groups that cannot be H-bonded to water molecules even at a highly humidified condition [32]. However, the diatom-silica (without thermal treatment) are found to have a structure containing $(SiO)_3$ ring, which can only be formed after thermally treatment for silica gel [13]. In this sense, the diatom-silica is more similar to the pyrogenic silica rather than the silica gel. These facts reflect that diatom-silica might possess some unique properties different from other amorphous silicas. More efforts focused on the silanols structure, as well as on the biomineralization process of diatom from the point of view of biochemistry [39] might be necessary to obtain a better understanding of diatom-silica.

From the present study, it can be concluded that removal of surface adsorbed water (including dehydration of liquid-like water followed by H-bonded capping water) in advance is crucial for the silylation of diatom-silica. A favorable pretreatment condition to remove adsorbed water and then to completely expose isolated silanols in this work is calcination at 1100 °C for 1 h. However, it is worth noting that the complete dehydration could be achieved at a much lower temperature (ca. 800 °C) by extending calcination time from 1 to 3 h, indicated by our experiment (not shown here). Hence, both temperature and time should be considered to achieve a feasible pretreatment in an industrial process.

The ^{1}H MAS NMR spectra of the pretreated diatom-silicas samples in a rehydration test are shown in Fig. 5 (a′)–(g′). It can be found that under a not very strict storage condition all of the pretreated samples are easily rehydrated, characteristic of the re-appearance of the strong signals (at ca. 4.9 ppm) of the liquid-like water (Fig. 5(a′)–(f′)). This result suggests that a strict control on the ambient humidity of container and a short storage time is indispensable for the silylation of diatom-silica in an industrial process.

4. Conclusions

The effects of pretreatment temperature on the surface silylation of diatom-silica by TMCS were investigated in this study. On the basis of the results derived from the combined analyses of chemical analysis, thermal analysis, ^{1}H MAS NMR, and FTIR, some novel findings can be summarized as follows:

(1) Before thermal pretreatment diatom-silica presents a high hydrated surface, in which most of silanols are covered with H-bonded water (i.e. capping water). And on the ground of capping water, there exists multiplayer of physisorbed water molecules with liquid-like structure. In this case the TMCS is hard to be grafted onto the surface of diatom-silica.

(2) An increase of the pretreatment temperature leads to the stepwise removal of physisorbed water followed by capping water, resulting in an increase of the amount of exposed silanols. Among these silanols, isolated silanols shows high reactivity in the silylation reaction with TMCS, in contrast with the H-bonded ones that shows poor reactivity. Basically, the degree of surface silylation of diatom-silica strongly depends on the amount of uncovered isolated silanols.

(3) Thermal pretreatment at 1100 °C for 1 h in ambient condition is found to be a favorable temperature to achieve a high degree of silylation (1.81 mmol/g of loaded TMCS to diatom-silica). However, a much lower pretreatment temperature for a desirable silylation is foreseeable in an actual industrial process by extending the time of pretreatment. On the other hand, strict control of the ambient humidity and short storage time are important to prevent the rehydration of the surface of diatom-silica.

References

[1] E.F. Stroermer, J.P. Smol, The Diatoms Applications for the Environmental and Earth Sciences, Cambridge University Press, Cambridge, 2001.

[2] S. Ek, A. Root, M. Peussa, L. Niinisto, Thermochim. Acta 379 (2001) 201.

[3] T. Takei, K. Kato, A. Meguro, M. Chikazawa, Colloid Surf. A 150 (1999) 77.

[4] C.E. Bronnimann, R.C. Zeigler, G.E. Maciel, J. Am. Chem. Soc. 110 (1988) 2023.

[5] M.L. Hair, W. Hertl, J. Phys. Chem. 73 (1969) 2372.

[6] B.A. Morrow, A.J. McFarian, Langmuir 7 (1991) 1695.

[7] B. Fubini, V. Bolis, A. Cavenago, E. Garrone, P. Ugliengo, Langmuir 9 (1993) 2712.

[8] V.I. Lygin, Russ. J. Gen. Chem. 71 (2001) 1368.

[9] Q. Zeng, J.F. Stebbins, A.D. Heaney, T. Erdogan, J. Non-Cryst. Solids 258 (1999) 78.

[10] A. Tuel, H. Hommel, A.P. Legrand, Langmuir 6 (1990) 770.

[11] C.C. Liu, G.E. Maciel, J. Am. Chem. Soc. 118 (1996) 5103.

[12] A.P. Legrand, H. Hommel, J.B. Caillerie, Colloid Surf. A 158 (1999) 157.

[13] B. Humbert, J. Non-Cryst. Solids 191 (1995) 29.

[14] D.W. Sindorf, G.E. Maciel, J. Am. Chem. Soc. 103 (1981) 4263.

[15] H. Gunther, S. Oepen, M. Ebener, V. Francke, Magn. Reson. Chem. 37 (1999) S142.

[16] F. Garbassi, L. Balducci, P. Chiurlo, L. Deiana, Appl. Surf. Sci. 84 (1995) 145.

[17] F. Bauer, A. Freyer, H. Ernst, H.J. Glasel, R. Mehnert, Appl. Surf. Sci. 179 (2001) 118.

[18] S. Azizi, T. Tajouri, H. Bouchriha, Polymer 41 (2000) 5921.

[19] H. Hamdan, M.N.M. Muhid, S. Endud, E. Listiorini, Z. Ramli, J. Non-Cryst. Solids 211 (1997) 126.

[20] L. Wang, Q. Nie, M. Li, F. Zhang, J. Zhuang, W. Yang, T. Li, Y. Wang, Appl. Phys. Lett. 87 (2005) 194105.

[21] R. Bertermann, N. Kroger, R. Tacke, Anal. Bioanal. Chem. 375 (2003) 630.

[22] A. Gendron-Badou, T. Coradin, J. Maquet, F. Frohlich, J. Livage, J. Non-Cryst. Solids 316 (2003) 331.

[23] P. Huttenloch, K.E. Roehl, K. Czurda, Environ. Sci. Technol. 35 (2001) 4260.

[24] X. Li, C. Bian, W. Chen, J. He, Z. Wang, N. Xu, G. Xue, Appl. Surf. Sci. 207 (2003) 378.

[25] P. Yuan, H.P. He, D.Q. Wu, D.Q. Wang, L.J. Chen, Spectrochim. Acta A 60 (2004) 2941.

[26] P. Yuan, D.Q. Wu, H.P. He, Z.Y. Lin, Appl. Surf. Sci. 227 (2004) 30.

[27] P. Yuan, D. Wu, Z. Chen, Z. Chen, Z. Lin, G. Diao, J. Peng, Chinese Sci. Bull. 46 (2001) 1118.

[28] E.F. Vansant, P. Van Der Voort, K.C. Vrancken, Characterization and Chemical Modification of the Silica Surface, Elsevier, Amsterdam, 1995.

[29] L.T. Zhuravlev, Langmuir 3 (1987) 316.

[30] L.T. Zhurvavlev, React. Kinet. Catal. Lett. 50 (1993) 15.

[31] F. Noll, M. Sumper, N. Hampp, Nano. Lett. 2 (2002) 91.

[32] J.-B. d'Espinose de la Caillerie, M.R. Aimeur, Y.E. Kortobi, A.P. Legrand, J. Colloid Interf. Sci. 194 (1997) 434.

[33] B. Humbert, A. Burneau, J. Non-Cryst. Solids 143 (1992) 75.

[34] J.A. Davis, D.B. Kent, Surface complexation modeling in aqueous geochemistry, in: M.F. Hochella, A.F. White (Eds.), Reviews in Mineralogy, Washington DC, 1990.

[35] X.S. Zhao, G.Q. Lu, A.K. Whittaker, G.J. Millar, H.Y. Zhu, J. Phys. Chem. B 101 (1997) 6525.

[36] B.H. Wouters, T. Chen, M. Dewilde, P.J. Grobet, Micropor. Mesopor. Mater. 44&45 (2001) 453.

[37] X.S. Zhao, G.Q. Lu, J. Phys. Chem. B 102 (1998) 1556.

[38] R.S. Mcdonald, J. Phys. Chem. 62 (1958) 1168.

[39] N. Kroger, R. Deutzmann, M. Sumper, Science 286 (1999) 1129.