Kinetics of interaction of 3-aminopropyltriethoxysilane on a silica gel surface using elemental analysis and diffuse reflectance infrared Fourier transform spectra

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In order to study the kinetics of interaction of 3-aminopropyltriethoxysilane (APTS) on silica gel, silica gel samples reacted with APTS were prepared by sampling the reaction mixture from the reactor at various time intervals, and the concentrations of 3-aminopropylsilyl (APS) groups modified on the silica gel surface were determined by elemental analysis. From the reaction time dependence of the APS concentration, it has been found that, after an initial fast reaction of APTS and silica gel, a slower second reaction and a much slower third reaction subsequently occur. For the three processes, the reaction rate constants (k_{obs}/s^{-1}) have been estimated and found to be $k_{obs}^{i} = 1.00 \times 10^{-1}$ s^{-1} for the initial reaction, $k_{obs}^{s} = 6.91 \times 10^{-3}$ s^{-1} for the second reaction and $k_{obs}^{t} = 4.20 \times 10^{-4}$ s^{-1} for the third reaction. The diffuse reflectance infrared Fourier transform (DRIFT) spectra were measured for the same samples. Bands at 3734–3739 cm^{-1} were observed in the OH stretch mode region, and were found to decrease in intensity with reaction time, reflecting the rate of reaction of APTS on the silica gel. Analysis of an OH stretching band has also furnished reaction rate constants that are very similar to those obtained from the time dependence of the APS concentration. A mechanism for the three reaction processes is postulated.

Although the surface properties of silica gel and its interactions with various adsorbates and reactants have been intensively investigated for more than four decades,[1] the surface structures of silica gel and organosilane-modified silica gel, in particular, remain topics of intense interest, because of the great significance of these gels in industrial applications.

A variety of experimental techniques have been used to characterize the surface of silica gel.[2–6] These studies conclude that the surface is covered with SiOH groups and that these surface hydroxy groups can be classified into two categories: 'free', which provide a narrow IR absorption band near 3750 cm^{-1}, and 'bound', which are characterized by a very broad IR absorption band in the 2800–3700 cm^{-1} region.
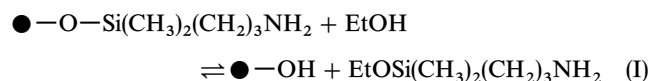
Davydov *et al.*[2] indicated the greater importance of free hydroxy groups in the reaction of trimethylchlorosilane (TMCS) and dimethyldichlorosilane (DMDCS) with the surface of silica. Snyder and Ward[7] pointed out the existence of reactive hydroxy groups, in addition to the free and bound hydroxy groups on the silica surface, and further indicated that although the surface varies widely, reactive hydroxy groups predominate on fine pore silicas. IR spectra of aerosol silica samples were investigated by Tsuchiya[8] and deconvolution of the absorbance difference spectra using a curve resolver showed that the resultant deconvoluted IR bands, arising from the SiOH groups, provide information about the structure and phenomena related to surface hydroxy groups.

Evans and White[9] used a gravimetric adsorption technique to obtain quantitative data on the interactions of methylchlorosilane vapours with the hydroxy groups of a silica surface. The results showed that adsorption of methylchlorosilanes at these hydroxy sites is physical and reversible at 30 °C, whereas at higher temperatures the hydroxy groups react with the methylchlorosilanes.

The kinetics of the reaction of mono-, di- and trimethylchlorosilanes with the free hydroxy groups on silica have been analysed at temperatures above 200 °C by Hair and Hertl.[10] The results indicate that while monomethylchlorosilane follows first-order kinetics, those for di- and trimethylchlorosilanes are at the order 1.5 ± 0.2.

Waddell *et al.*[11] measured the absorbance at λ_{max} (404 nm) for the yellow Schiff's base formed by reacting salicylaldehyde with (aminopropyl)silanes either in solution or on the surface of silica and found that this technique provided an excellent means of measuring the relative stability of the silanes bound onto the surface. They also examined the kinetics for the reversible reaction as shown in reaction (I) (where ● represents the surface of the silica gel).

$$\bullet-O-Si(CH_3)_2(CH_2)_3NH_2 + EtOH$$
$$\rightleftharpoons \bullet-OH + EtOSi(CH_3)_2(CH_2)_3NH_2 \quad (I)$$

The absorbance of samples removed after 0, 1, 3 and 6 days of reactivity reflected reversible pseudo-first-order kinetics.

The thermometric enthalpy titration study by Kelly and Leyden[12] of the interaction of 3-aminopropylsilane on the surface of silica gel in an aqueous slurry with HClO$_4$ provides significant information about the behaviour of NH$_2$ groups that participate in hydrogen bonding in reaction within the silane species attached to the surface.

The distribution and reactivity of the different hydroxy species that exist on the surface of the silica gel have been studied by Van der Voort *et al.*[13] by using Fourier-transform IR spectroscopy with photoacoustic detection. These studies led to the conclusion that the reactivity of the free hydroxy groups with trichlorosilane is not affected by the polar radius, whereas the vicinal hydroxy groups become less reactive towards trichlorosilane as the pore radius decreases. The vibrational spectra of silica samples activated in vacuum in the temperature range 450–800 °C were subsequently investigated in detail by Morrow and McFarlan.[14] They showed the

existence of two types (I and II) of isolated hydroxy species, and although type I are truly isolated, those of type II remain a weakly interacting vicinal pair.

Chiang et al.[15] reported a structural study of a 3-aminopropyltriethoxysilane (APTS) layer formed on silica gel, and concluded that while the hydrolysed aminosilane adsorbs onto the silica gel almost as a monolayer, the amino groups interact with the silica surface.

A detailed study of the effect of water molecules in the reaction of APTS with silica gel has been made by Vrancken et al.[16] using diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy and cross-polarization magic-angle-spinning (CP MAS) NMR spectroscopy. The results of both techniques led to the postulate of the presence of four modified structures on the silica surface, their nature depending on the conditions used. Then they further studied the role of APTS in the modification of silica with silanes using these two techniques.[17] Results of special relevance to this study are: first, the hydroxy groups are formed as a result of hydrolysis of the silane ethoxy groups and can form hydrogen bonds with the surface hydroxy groups; and second, a hydroxy group can react with a silica surface hydroxy group or the hydroxy group of a neighbouring silane molecule to form a siloxane bond.

It is, therefore, abundantly clear that hydroxy groups play a critical role in consolidation of a silane coating onto a gel surface. However, in spite of the important relationship of silane modification with problems associated with the interfacial reinforcement of advanced materials, the mechanism for this reaction has not been clearly elucidated. Further investigation of silane modification on the surface of silica gel is therefore highly desirable.

Murthy and Leyden[18] made a very important quantitative investigation of the concentration of the organosilane layer modified on silica using DRIFT spectroscopy. They investigated the effect of the silica gel particle size on the DRIFT spectrum, and found that they could use the band at 1870 cm^{-1} as a reference as the intensity of this SiO combination band was almost unaffected by particle size.

Nishio et al.[19] measured the DRIFT spectra of silica gel reacted with γ-anilinopropyltrimethoxysilane and discussed the structure of the silane layer coating the surface. They also investigated the dehydration condensation of tetramethoxysilane (TMS) on tin(IV) oxide particles,[20] and showed that a higher concentration of the TMS solution favours formation of siloxane bonds.

Recently, Vrancken et al.[21] have suggested that the surface modification reaction of silica gel with aminoorganosilanes proceeds in two steps (the reaction step and the curing step) and that the deposition of the aminosilane molecules is governed by the area and hydration of the surface.

In the present study, three different experimental techniques (^{29}Si CP MAS NMR, DRIFT spectroscopy and elemental analysis) have been used to study samples of APTS-modified silica gel. Three separate reaction steps have been identified. In particular, data obtained by sampling the substrates from the reaction vessel at various short time intervals have enabled us to discuss, for the first time, the kinetics of a fast reaction of APTS with the surface of silica gel. We also emphasize that in contrast to the earlier results of Waddell et al.,[11] data from elemental analysis reflect irreversible kinetics for the reaction system as the samples were completely quenched after sampling and a reversible reaction was not possible under the reaction conditions.

Experimental

Materials

Super Micro Bead Silica Gel B-5 (SMBS), with a particle size

distribution of $d_{10}/d_{90} = 1.5$, average particle diameter 5 μm and pore diameter 5.5 nm, was purchased from Fuji Silysia Chemical Co. Surface areas (498 $m^2 g^{-1}$) were determined by the BET method using nitrogen adsorption (16.2 $Å^2$ assumed for molecular N_2). APTS was purchased from Shinetsu Chemical Industry Ltd., and was used without further purification.

SMBS–APTS reactions

SMBS samples modified with APTS were prepared as follows. SMBS (40 g) in toluene (120 ml) was refluxed with stirring at 423 K. APTS (0.08–0.72 mol l^{-1}) was added to the preheated SMBS–toluene mixture, and refluxed for 6 h with stirring (under these conditions the reaction was completed). The SMBS–APTS–toluene mixture, separated from the reactor, was washed with methanol to quench the reaction. Unreacted ethoxy groups in the substrate were hydrolysed in water–methanol (1:1) for 2 h at room temperature. The APTS-modified SMBS was again washed with methanol and dried at 388 K under vacuum. Thus, six samples modified with different APTS concentrations were prepared (samples A; A-1–A-6). A sample of SMBS treated under the same conditions but in the absence of APTS was also prepared (sample A_0, control). These samples A can be regarded as the APTS–SMBS complexes prepared under equilibrium conditions.

The rate of reaction of APTS with SMBS was followed by removing samples of the APTS–SMBS product from the reactor at various time intervals. The concentration of APTS in the toluene solution was 0.50 mol l^{-1}, and the temperature of the reaction was 388 K. Each extract was treated as described above, and the samples thus prepared were dried at 388 K under vacuum. Samples B (B-1–B-7) were obtained at time intervals of 60, 180, 300, 600, 900, 1 800 and 21 600 s, respectively. The methanol used for washing the samples was removed by evaporation until the IR bands arising from methanol could no longer be detected. These samples were not heated above 388 K, and were therefore assumed to be in a fully hydrated state.

Elemental analysis

A Yanaco-CN Coder MT 600 was used for elemental analysis of the samples. The concentration of APTS reacted with the silica gel was determined by analysing the nitrogen content of the samples. The error was ±0.3%.

DRIFT spectroscopic measurements

DRIFT spectra were recorded on a Nicolet Magna System 750 at 4 cm^{-1} resolution using the Spectra Tech Collector diffuse reflectance accessory at room temperature. Samples were mixed with dried KBr and were used to fill the DRIFT sample cup before measurement.

^{29}Si NMR measurements

The ^{29}Si NMR spectra were recorded on a Varian UNITY-400 spectrometer operating at 79.5 MHz at 25 °C. The ^{29}Si chemical shifts (δ) are given relative to an external 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) standard. The high-resolution solid-state ^{29}Si NMR measurements were achieved by cross-polarization sequence (XPOLAR). The ^{29}Si NMR spectra were measured using an acquisition time of 0.102 s, a contact time of 2.5 ms, a recycle time of 15 s, and a pulse width of 6.3 μs. The spectra with CP (designated CP herein) were measured by cross-polarization and magic-angle-spinning (CP MAS). The spectra without CP were measured using only MAS (designated NCP). In order to determine the recycle time, the spin-lattice relaxation time (τ_1) of the CP MAS spectra and that of the NCP (MAS) spectra were mea-

sured [5 s for the CP MAS τ_1 value and 11 s for the NCP (MAS) τ_1 value]. Furthermore, several contact times for the NMR measurement were tried and a contact time of 2.5 ms was determined to be the most suitable. The two types of spectra were integrated and then the CP correction factors[17] were obtained from division of the NCP integral values by the CP integral values for each resonance line. Thus, the real integral values were calculated from multiplication of the CP integral values with the CP correction factors (the correction factors were 0.27, 0.30, 0.46 and 0.97 for the ^{29}Si resonance lines of sample A-6 at $\delta = -62$, -70, -104 and -115, respectively).

Results and Discussion

Determination of the number of SiOH groups by ^{29}Si NMR techniques

Fig. 1 shows a representative ^{29}Si CP MAS NMR (79.5 MHz) spectrum of sample A-6 in the solid state. The resonance signals 1, 2 and 3 at $\delta = -52$, -62 and -70 arise from the ^{29}Si nuclei of the APS moieties bound on the SMBS particles, and are ascribed to the ^{29}Si nuclei of the $(-O)Si(OH)_2C-$, $(-O)_2Si(OH)C-$ and $(-O)_3SiC-$ groups, respectively.[18,22] A very weak signal (4) at $\delta = -93$ and the ^{29}Si NMR signals (5 and 6), observed at $\delta = -104$ and -115, come from the SMBS particles and are assigned to the ^{29}Si nuclei of the $(-O)_2Si(OH)_2$, $(-O)_3SiOH$ and $(-O)_4Si$ groups, respectively.[18,22] We can assume that for the three signals at $\delta = -93$, -104 and -115 the total integral intensities corrected by the CP correction factors $(I_4 + I_5 + I_6)$ are independent of the amount of bound APS, as these signals arise from the ^{29}Si nuclei belonging only to the SMBS particles. For the controlled SMBS particles, the integral intensity ratio of these three signals, corrected by the CP correction factors, were found to be 2.14 : 48.88 : 8.98, showing that the population of geminal hydroxy species $[(-O)_2Si(OH)_2]$ is very small. However, for the three signals arising from only bound-APS,

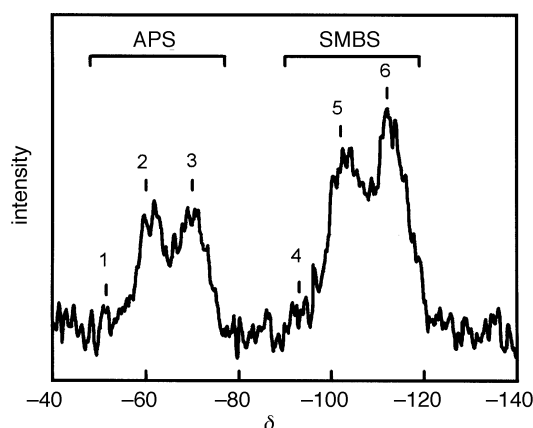**Table 1** Elemental analysis data and concentration of modified APS for samples A

sample	C_N (wt.%)	$C_{APS}/\mu mol\ m^{-2}$
A-1	0.25 ± 0.3	0.36
A-2	0.56 ± 0.3	0.74
A-3	0.76 ± 0.3	1.01
A-4	1.02 ± 0.3	1.81
A-5	1.47 ± 0.3	3.27
A-6	1.66 ± 0.3	3.36

it may be assumed that the total corrected integral intensities $(I_1 + I_2 + I_3)$ depend upon the amount of APTS reacted with the SMBS. If we put the total corrected integral intensities $(I_4 + I_5 + I_6)$ equal to 100, then we can describe the total relative integral intensities of those ^{29}Si signals (I_{APS}) for the APS moieties relative to the value $(I_1 + I_2 + I_3)/(I_4 + I_5 + I_6) = I_{APS}/100$. The concentrations of bound APS for samples A were determined by elemental analysis (nitrogen content) and are listed in Table 1. The relative corrected integral intensity of each species for samples A is listed in Table 2 together with the concentration (per unit area) of bound APS. These relative corrected integral intensities should be proportional to the concentration of bound APS. As shown in Fig. 2, a linear relationship does exist.

Hence, we can estimate quantitatively the APS concentration per unit area from both the relative corrected integral intensities and the modified APTS quantities. Similarly, the concentrations of the $(-O)_3SiOH$ and $(-O)_4Si$ species belonging to the SMBS particles can be calculated by the use of reduction coefficients $[(C/\mu mol\ m^{-2})$ relative corrected

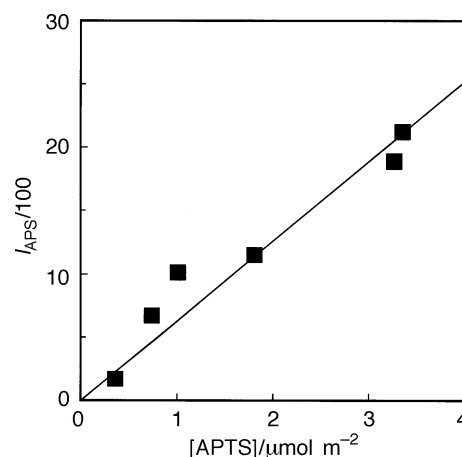**Fig. 1** ^{29}Si CP MAS spectrum of sample A-6 at 25 °C

Fig. 2 Plot of corrected integral intensity of the APS derived ^{29}Si resonance signals against the concentration of APS modified for samples A

Table 2 Corrected integral intensities of the ^{29}Si resonance lines for the modified APS, $(-O)_3SiOH$ and $(-O)_4Si$ species and concentrations of the three species calculated from the NMR data

sample	corrected integral intensity (%)			C/molecules nm^{-2}		
	APS	$(-O)_3SiOH$	$(-O)_4Si$	C_{APS}	$C_{(-O)_3SiOH}$ (α_{OH})	$C_{(-O)_4Si}$
A-1	1.68	42.54	57.46	0.16	4.07	5.50
A-2	6.69	41.86	58.14	0.64	4.01	5.57
A-3	10.07	34.47	65.53	0.96	3.30	6.27
A-4	11.46	30.58	69.42	1.10	2.93	6.65
A-5	18.89	32.93	67.07	1.81	3.15	6.42
A-6	21.21	27.08	72.92	2.03	2.59	6.98

integrated intensity for each peak of APS]. The concentration of the ($-$O)$_3$SiOH species corresponds to the number (α_{OH}) of silanol OH groups (the geminal hydroxy species are neglected due to their very low concentration). The calculated ($-$O)$_3$SiOH and ($-$O)$_4$Si concentrations are listed in Table 2. When the concentration of APS bound on the silica surface increases, it is found that the concentration of the ($-$O)$_3$SiOH species decreases while that of the ($-$O)$_4$Si species increases. This observation shows directly that the reaction of the ($-$O)$_3$SiOH species with the APTS molecules brings about an increase in the number of the ($-$O)$_4$Si species. For unmodified SMBS particles (control samples), the concentrations of the ($-$O)$_3$SiOH and ($-$O)$_4$Si species can be estimated by extrapolating the APS concentration to zero in plots of APS concentration against α_{OH}. The α_{OH} value (4.41) of the control SMBS particles obtained is very close to that (4.7) of silica gel (Kieselgel 60), as reported by Vrancken et al.[17]

As can be seen in Table 2, the difference (1.87 molecules nm^{-2}) in the concentrations of bound APS between the A-1 and A-6 samples is not equal to that (1.48 molecules nm^{-2}) in the ($-$O)$_4$Si concentrations on the surface of silica gel for these two samples. If condensation occurs between one APTS molecule and one silica gel hydroxy group, then these two differences should be equal. Their inequality, therefore, implies that 21% of the APS concentration of sample A-6 could be the consequence of a reaction between the APTS molecules (i.e., the concentration is not restricted by reaction between one hydroxy group on the surface of the silica gel and one APTS molecule). Thus, we may assume that 79% of bound APS segments in sample A-6 have two hydroxy groups while the remaining 21% have an average of one hydroxy group.

Concentration effect of modified APTS on the ν_{OH}^{Si} band

Fig. 3(A) shows the DRIFT spectra of sample A-6 and of the control SMBS particles. An IR band at 3739 cm^{-1} observed for SMBS is very close to that (3743 cm^{-1}) of silica gel reported by Vrancken et al.,[17] and is assigned to an OH stretching mode (ν_{OH}^{Si}) arising from the SiOH groups on the SMBS particles. The IR bands observed for samples A in the 3700–3750 cm^{-1} region are also assigned to the ν_{OH}^{Si} vibrational modes of unreacted hydroxy groups on the silica-gel surface.

For dry silica gel, four bands at 3749, 3742, 3720 and 3500–3700 cm^{-1}, arising from four different types of surface hydroxy groups, have been observed by van Roosmalen and Mol,[23] and the former two bands have been assigned to isolated and geminal hydroxy groups, respectively.

The ν_{OH}^{Si} band observed at 3739 cm^{-1} for the control SMBS particles is at a lower frequency, compared with that for dry silica gel, and is derived from the fully hydrated state of SMBS.

In the DRIFT spectra of samples A [Fig. 3(B)], it is found that the ν_{OH}^{Si} band shifts to low frequency and that the band intensity decreases as the concentration of bound APS increases. Therefore, we can assume that the band shift is induced by the bound APS moiety and a decrease in intensity comes from consumption of hydroxy groups in the APTS–SMBS reaction. In particular, the shift in frequency is not as obvious at large α_{OH}/C_{APTS} ratios ($\geqslant 5.4$), although it is pronounced at smaller ratios (< 5.4). Therefore, one can estimate that the origin of the lowering in frequency shift comes about from formation of hydrogen bonds between the APS–NH$_2$ and SMBS–SiOH groups.[15,22]

Participation of the APS–NH$_2$ groups in hydrogen-bond formation is reflected directly in the NH$_2$ vibrational modes. When the APTS molecules are in the monomer state in toluene, two IR bands at 3384 and 3324 cm^{-1} are observed and are assigned to the asymmetric and symmetric NH$_2$ stretch modes ($\nu_{NH_2}^{asy}$ and $\nu_{NH_2}^{sym}$), respectively.[24] However, in the APS-bound SMBS samples, the two vibrational modes are

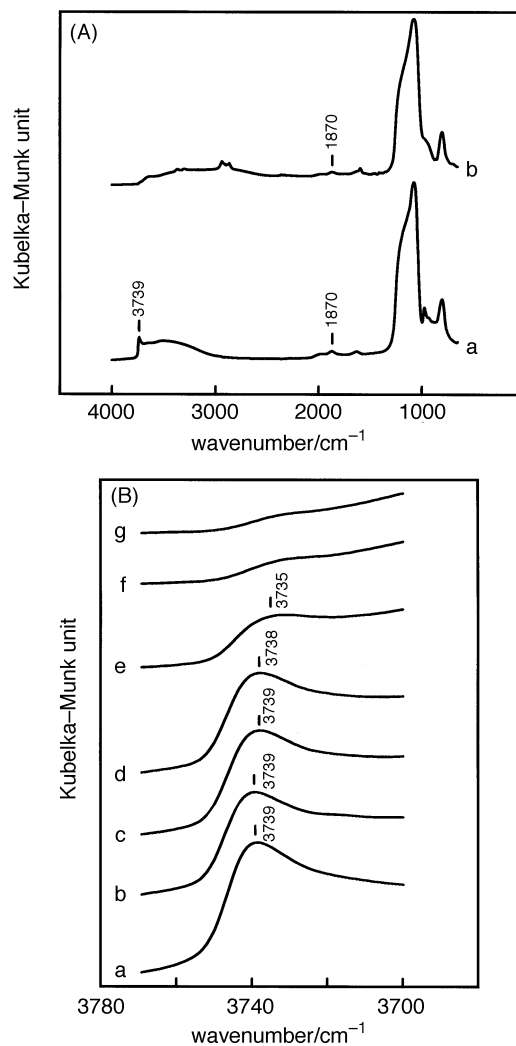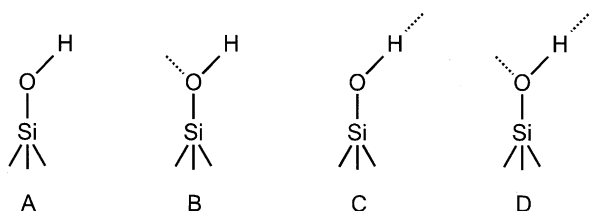**Fig. 3** (A) DRIFT spectra of: a, sample A-6 and; b, control SMBS in the 700–4000 cm^{-1} region. (B) DRIFT spectra of: a, control; b, A-1; c, A-2; d, A-3; e, A-4; f, A-5; and g, A-6 in the ν_{OH}^{Si} mode region at 25 °C. The SiO combination band at 1870 cm^{-1} may be used as a reference band.

observed at lower frequencies, as shown in Fig. 4. For the DRIFT spectra of samples A in the NH-stretch region, the asymmetric and symmetric NH$_2$ stretch modes appear at 3368–3375 and 3304–3313 cm^{-1}, respectively. For samples A with lower APS concentrations, the asymmetric NH$_2$ stretch bands appear at 3375 cm^{-1}, while for those with higher APS concentrations they are observed at lower frequencies (3368 cm^{-1} for sample A-6). Dependence of the $\nu_{NH_2}^{sym}$ mode on the APS concentration is even more pronounced. For samples with low APS concentration, predominant bands at 3311–3313 cm^{-1} and shoulder bands at 3304–3305 cm^{-1} are observed. However, for the sample with a high APS concentration, it is seen that the 3304–3305 cm^{-1} band now becomes predominant while the 3311–3313 cm^{-1} band appears as a shoulder, indicating that the APS–NH$_2$ groups mainly participate in two different hydrogen-bonding environments. Formation of hydrogen bonds is possible between the silanol–OH and APS–NH$_2$ group or between the two APS–NH$_2$ groups. However, we can assume that the former is dominant, since there is a correlation between the ν_{OH}^{Si} band frequency and the concentration of bound APS. Thus, the DRIFT spectra in the ν_{OH}^{Si} and ν_{NH_2} regions provide evidence for hydrogen bonding between APS–NH$_2$ and silica-gel–SiOH groups.

Hydroxy groups on the surface of the silica gel can be classified into four types,[8] and are represented schematically with respect to single silanol groups as follows:

The frequencies of the v_{OH}^{Si} bands corresponding to the four types should decrease in the order A > B > C > D.[8] The v_{OH}^{Si} band of the type B hydroxy group should be located near the v_{OH}^{Si} band of type A. For geminal silanol groups, four similar types can also be considered.

Tsuchiya[8] has shown that the IR band arising from the type A silanol is found at 3745 cm^{-1} and that of the type B hydroxy group at 3731 cm^{-1}. For silica gel in the hydrated state, we might expect the hydrogen-bonding environment on the silica surface to bring about an increase in type-B population. Recently, Vrancken et al.[17] assigned the band maximum at 3743 cm^{-1} for silica gel to the free single and geminal silanols, and the second band at 3731 cm^{-1}, which was observed for silica bound with APS in aqueous conditions, to silane hydroxy groups. For APS-bound silica gel, it can be assumed that the hydrolysed silane silanols remain uncondensed and form type B hydrogen bonds with surface silanols or neighbouring silane hydroxy groups.

When the amount of bound APS increases, the NH$_2$ group of APS probably forms hydrogen bonds at the oxygen atom of free single (or minor geminal) hydroxy groups, thereby leading to an increase in the number of type-B hydroxy groups. This may cause a lowering in frequency shift of the v_{OH}^{Si} band, which is observed for the APS–SMBS complexes.

Moses et al.[25] have suggested that an internal hydrogen bonded six-membered ring structure exists for aminosiloxane and Chiang et al.[15] have proposed a hydrogen bonding model of the SiO$^-\cdots$H—N$^+$H$_2$ type on the surface of silica gel. However, since the hydrogen atom in both these models would be perturbed, an OH-stretching mode should be observed at a much lower frequency.

We have focused, in particular, on the intensities of the v_{OH}^{Si} bands at 3734–3739 cm^{-1} relative to that of the SiO combination band at 1870 cm^{-1} [$R_{3734-3739} = (I_{3734-3739}/I_{1870})$] and have investigated in detail the effect of concentration of bound APS on the relative intensities. The
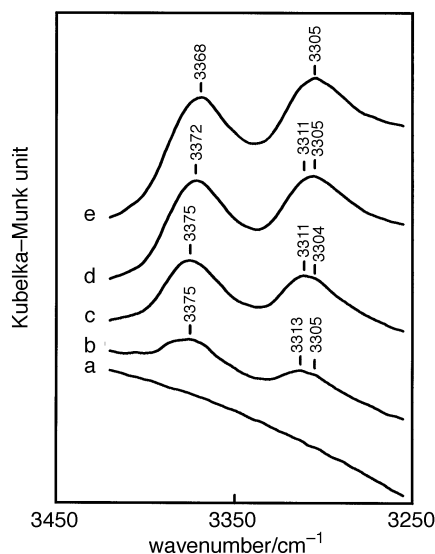
values of $R_{3734-3739}$ were found to decrease linearly as the amount of bound APS increases. This fact reveals that the differences (ΔR) between the relative intensity of the 3739 cm^{-1} band for the control SMBS and those of the v_{OH}^{Si} bands for the APS-bound samples correspond to the relative intensities of the v_{OH}^{Si} bands for the hydroxy groups that were consumed in the condensation reaction with the APTS molecules. As is shown in Fig. 5, the ΔR values are proportional to the concentration of modified APTS. Those of samples A5 and A6 deviate from the linear relationship. This might be caused by the fact that a higher APTS concentration was used for preparation of these samples and that relative intensities of the v_{OH}^{Si} bands arising from the unreacted SiOH groups are very small. From the ^{29}Si NMR results we can infer that the ΔR values, which are proportional to the APS concentration, probably reflect the intensities of the v_{OH}^{Si} bands coming from the two hydroxy groups of bound APS. The values that deviate from the linear relationship reflect those of an OH-stretching band of bound APS on molecules that have fewer than two hydroxy groups. In other words, as the number of hydroxy groups that remain unreacted in the process directly contributes to the value of ΔR, deviation from the linear relationship implies a change in the number of hydroxy groups involved in the process (see Fig. 6). In the linear region of the plots, we can, therefore, evaluate quantitatively the relative intensity of the v_{OH}^{Si} band for the hydroxy groups that react with a unit concentration of APTS. We can conclude that the relative intensity variation in the v_{OH}^{Si} band is a quantitative reflection of the condensation reaction between APTS and SMBS hydroxy groups.

Kinetics of the APTS molecules on SMBS

In order to follow the rate of the condensation reaction between APTS and SMBS, samples B were prepared by sequentially sampling the reaction mixture at various time intervals. The concentrations of bound APS were determined by elemental analysis (nitrogen content) and are listed in Table 3. It is found that the concentration of APS on the silica-gel surface increases with an increase in reaction time and reflects the kinetics of the irreversible silane–silica gel reaction. It should be noted that ca. 50–60% of the total APS bound at equilibrium (C_∞ at $t = \infty$) was modified at the time of first sampling (60 s).

The time dependence of the APS concentration (C) can be expressed by eqn. (1),

$$dC/dt = k(C_\infty - C) \qquad (1)$$

where k is the reaction rate constant, and C_∞ is the APS concentration bound on the silica-gel surface at equilibrium
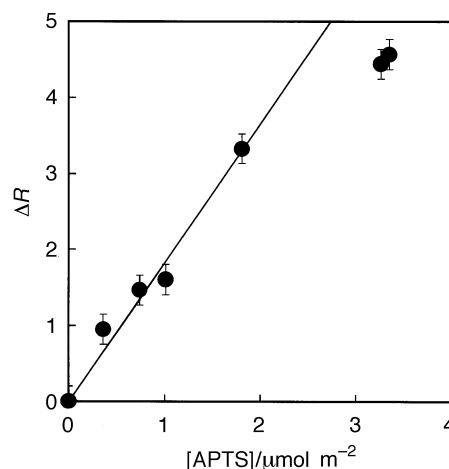

Fig. 4 DRIFT spectra of: a, control; b, A-2 ; c, A-4 ; d, A-5; and e, A-6 in the NH$_2$ stretch mode region at 25 °C

Fig. 5 Plots of ΔR against concentration of APS modified for samples A

(A) 1st process

(B) 2nd process
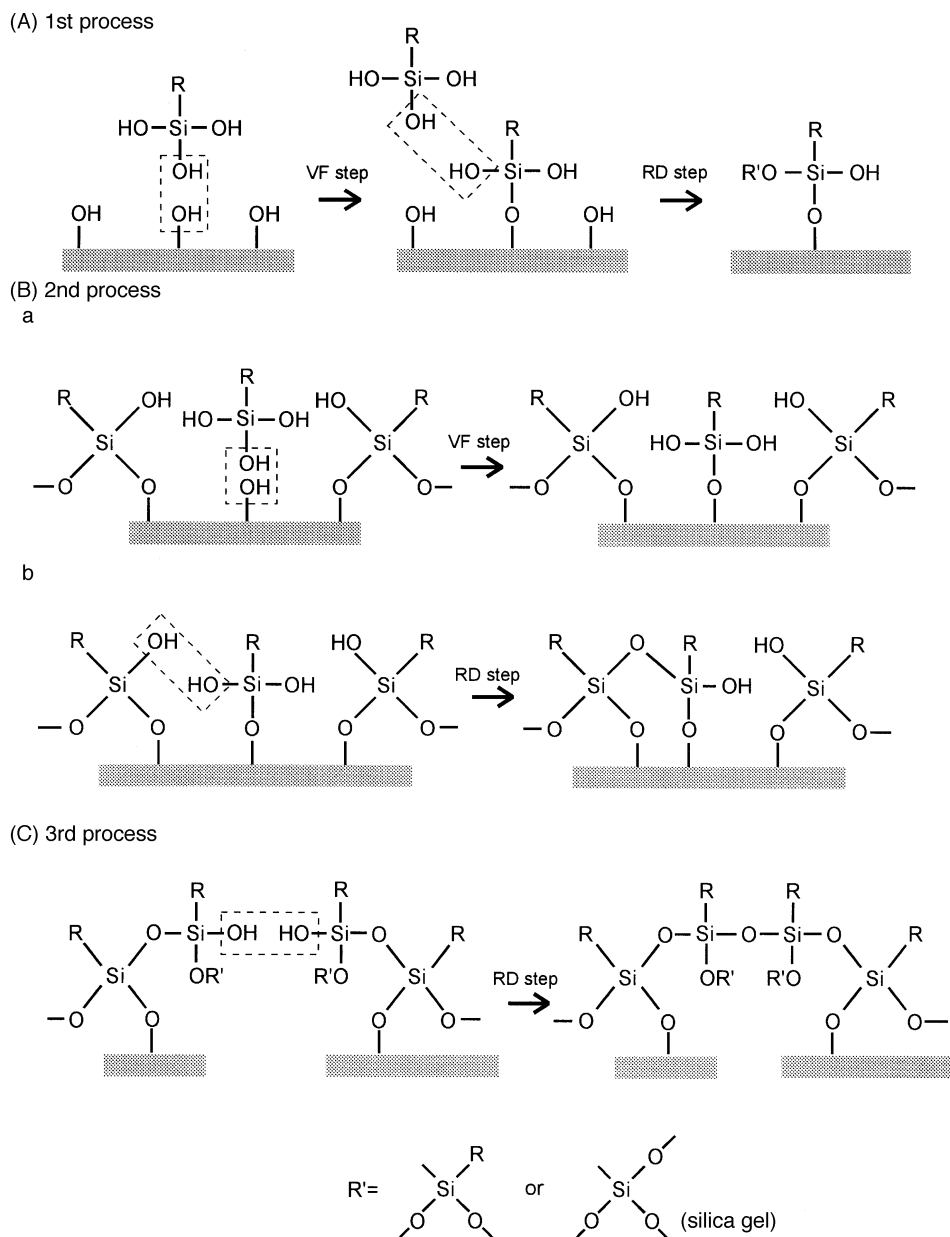
a

b

(C) 3rd process

R'= ... or ... (silica gel)

Fig. 6 Schematic models for the three reaction processes (VF step = very fast step; RD step = rate determining step)

$(t = \infty)$, which can be obtained by extrapolating to $t = \infty$ in the C vs. $1/t$ plots. Eqn. (1) can be reduced to eqn. (2),

$$-\ln[(C_\infty - C)/(C_\infty - C_0)] = kt \qquad (2)$$

where C_0 is the APS concentration on the silica gel surface at $t = 0$ $(C_0 = 0)$. For samples B, plots of $-\ln[(C_\infty - C)/(C_\infty - C_0)]$ vs. reaction time (t) are nonlinear, as shown in Fig. 7(A). The nonlinear relationship can be accounted for successfully by assuming that an initial fast

reaction is followed by a slower second reaction and a much slower third reaction.

In the plots of $-\ln[(C_\infty - C)/(C_\infty - C_0)]$ vs. t obtained from the nitrogen content data, we can assume that this third reaction follows the straight line A [Fig. 7(A)]. The differences between the values on line A and the plotted data provide data for calculation of line B for a slower second reaction [Fig. 7(B)], and consequently, the differences between the data on line B and a straight line drawn between O and P allow us to draw line C [Fig. 6(C)] for an initial fast reaction. Line C can be interpreted as being the initial tangent to the curve which represents the overall rate of reaction. As such, it reflects the rate constant of an initial fast reaction and the seeming absence of points in this region is not of concern.

The initial concentration (C_0) of APS for each reaction can be calculated from the zero-time intercepts in the plots of $-\ln[(C_\infty - C)/(C_\infty - C_0)]$ vs. t. The total concentration of APS bound on the SMBS surface for each reaction process will then be equal to the value of $C_\infty - C_0$. The slopes of these plots provide the apparent reaction rate constants (k_{obs}) for each reaction process equal to $k_{obs}^i = 1.00 \times 10^{-1}$ s^{-1} for the initial reaction, $k_{obs}^s = 6.91 \times 10^{-3}$ s^{-1} for the second reaction and $k_{obs}^t = 4.20 \times 10^{-4}$ s^{-1} for the third reaction.

Table 3 Elemental analysis data and concentration of modified APS for samples B

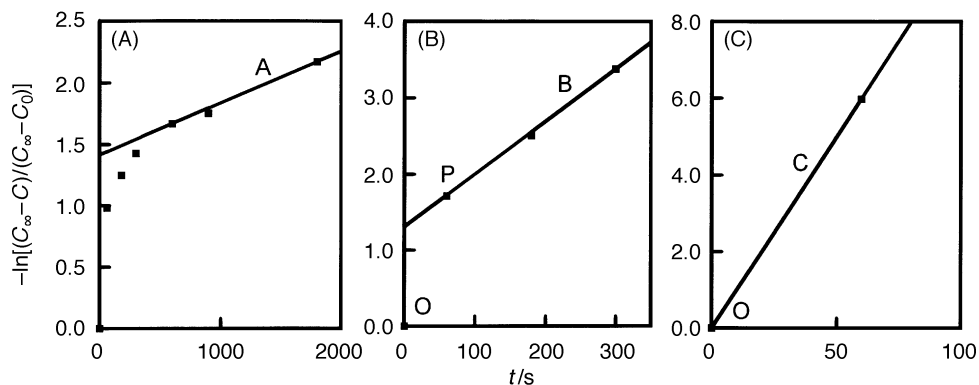| samples	t/s	C_N (wt.%)	$C_{APS}/\mu mol\ m^{-2}$
B-1	60	1.04 ± 0.3	1.59
B-2	180	1.17 ± 0.3	1.81
B-3	300	1.24 ± 0.3	1.93
B-4	600	1.32 ± 0.3	2.06
B-5	900	1.34 ± 0.3	2.10
B-6	1800	1.43 ± 0.3	2.25
B-7	21600	1.60 ± 0.3	2.55

Fig. 7 Plots of $-\ln[(C_\infty - C)/(C_\infty - C_0)]$ against reaction time (t/s) for samples B: (A) third process; (B) second process; (C) initial process. The intercepts of lines A and B provide the C_∞ values of the second- and third-reaction processes, respectively.

We can then compare the magnitude of these k_{obs} values for the three reaction processes. The rate constant for the second reaction process is *ca.* 16 times faster that of the third reaction, while that for the initial reaction is *ca.* 15 times faster than that for the second reaction.

Representative DRIFT spectra of samples B in the v_{OH}^{Si} mode region are shown in Fig. 8 together with that of the control sample of SMBS. Broad v_{OH}^{Si} band appears at 3734–3737 cm^{-1} and the band intensities decrease as the reaction time increases, implying that the rate of the APTS–SMBS reaction is reflected in these bands.
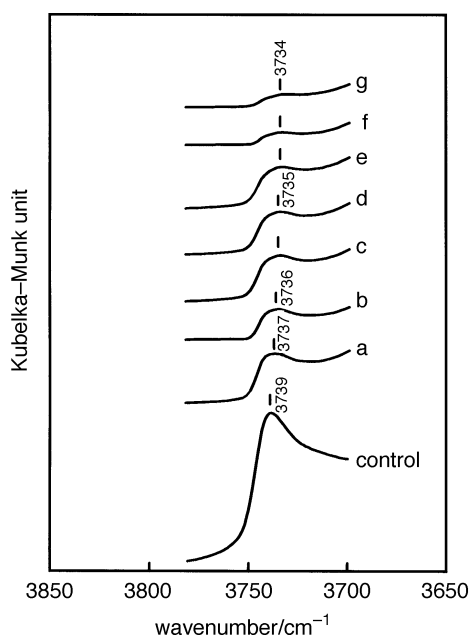
Fig. 8 DRIFT spectra of: a, B-1; b, B-2; c, B-3; d, B-4; e, B-5; f, B-6; and g, B-7 in the v_{OH}^{Si} mode region
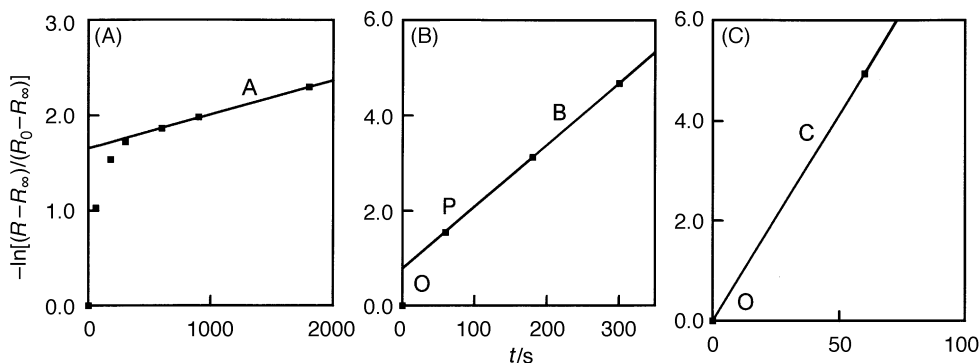
The time dependence of the relative intensity for each band can be expressed by eqn. (3),

$$-\ln[(R - R_\infty)/(R_0 - R_\infty)] = kt \qquad (3)$$

where k is the reaction rate constant, R_∞ is the relative intensity for each band at equilibrium ($t = \infty$), determined by extrapolation to $t = \infty$ in the R *vs.* $1/t$ plots, and R_0 is the relative intensity of each band at $t = 0$ ($R = R_0$ for the v_{OH}^{Si} band in the control sample of SMBS). The values of $-\ln[(R - R_\infty)/(R_0 - R_\infty)]$ for each band are plotted against reaction time in Fig. 9. The nonlinear relationship thus obtained [Fig. 9(A)] can also be explained by assuming three reaction processes. The reaction rate constants for the three processes are $k_{obs}^i = 0.82 \times 10^{-1}$ s^{-1} for the initial reaction, $k_{obs}^s = 1.30 \times 10^{-2}$ s^{-1} and for the second reaction, and $k_{obs}^t = 3.57 \times 10^{-4}$ s^{-1} for the third reaction. These values are similar to those evaluated from the time dependence data of bound APS (Fig. 7).

We can assume, however, that the third reaction process that we have observed corresponds to the reversible pseudo-first-order reaction reported by Waddell *et al.*,[11] and to the curing step proposed by Vrancken *et al.*[21]

Reaction mechanism

In this present study, the product samples of the APTS–SMBS reaction, prepared by sequentially sampling the reaction mixture at various time intervals, were thoroughly washed with methanol before they were dried and could therefore be considered to be free of physically adsorbed APTS. Therefore, the v_{OH}^{Si} band features of the B samples are a direct reflection of the variation in the environment of the SiOH group in a solid sample of an APTS–SMBS complex.

For the bands at 3734–3737 cm^{-1} of samples B, the values of ΔR are plotted (Fig. 10) against the quantity of APS bound in each reaction process. The plots consist of two linear portions, lines AB and BC, which correspond to the processes containing both the initial and second reactions, and the third
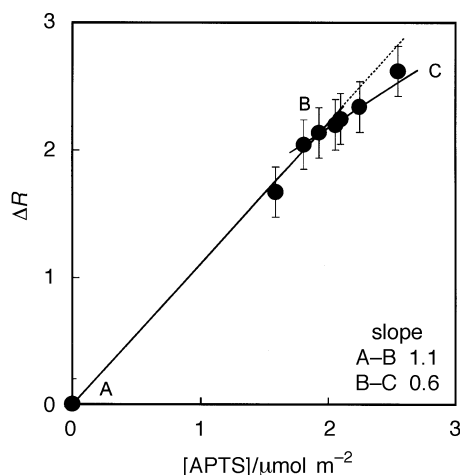
Fig. 9 Plots of $-\ln[(R - R_\infty)/(R_0 - R_\infty)]$ against reaction time (t/s) for the v_{OH}^{Si} bands of samples B: (A) third process; (B) second process; (C) initial process

Fig. 10 Plots of ΔR against modified APS concentration for samples B

reaction process, respectively. An overall nonlinear relationship probably arises because the number of hydroxy groups participating in the reaction between APTS and SMBS strongly depends upon the reaction time.

In turn, the slopes obtained from the two linear portions (Fig. 10) reflect the number of hydroxy groups that participate in the reaction process, as the slopes are in a ratio relative to the intensities for the hydroxy groups which react with unit concentration of APTS. We can assume that the intensity of the v_{OH}^{Si} band coming from bound-APS segments with the two hydroxy groups is the major contributor to the ΔR value in the linear portion AB, and that deviations from the linear relationship are caused by an increase in the concentration of bound APS with fewer than two hydroxy groups. In the initial and second processes, each of the APS segments bound onto the surface of silica gel probably has a dominance of two hydroxy groups. In the third process, condensation among APTS molecules brings about an increase in the concentration of APS segments with an average of one hydroxy group, which then react to give an increase in the population of APS segments with fewer than two hydroxy groups per segment. Thus, the two slopes, which are in the ratio 1.1 : 0.6, imply that the number of the hydroxy groups condensed in the initial and second reactions is approximately twice that condensed in the third reaction. From such time-dependent v_{OH}^{Si}-band data, we can discuss a mechanism for the three processes.

Schematic models are shown in Fig. 6. In the initial fast reaction [Fig. 6(A)], we can assume that the condensation reaction between one of the APTS hydroxy groups and the silica gel hydroxy group is very fast (designated the VF step) and that the reaction between one of the two hydroxy groups remaining uncondensed in a bound-silane molecule and the silica gel hydroxy group (or APTS hydroxy group) is rate determining (the RD step). Indeed, for the ^{29}Si CP MAS spectra of the samples B, the ^{29}Si resonance line at $\delta = -52$ arising from the geminal type $(-O)Si(OH)_2C$ species is very weak in intensity and the resonance lines due to the $(-O)_2Si(OH)C$ and $(-O)_3SiC$ species are predominant, supporting the model of an initial fast reaction.

In the second reaction [Fig. 6(B)], unreacted APTS molecules may be incorporated into the molecular gap in the first APS layer and may then react with a reactive hydroxy group of silica gel. The APS moiety, thus bound on the silica surface, still has two reactive hydroxy groups for extended condensation. Extended condensation among the unreacted hydroxy groups of the silane molecules bound on the surface occurs and formation of new siloxane bonds $(Si-O-Si)$ results in a

network of oligomerized silane molecules. This last reaction might be rate determining.

In the third reaction process, the subsequent reaction in the growth process from oligomer layer to polymerized multilayer becomes rate determining, since some hydrolysed silane silanols might remain unreacted in the oligomer layer.

In the above mechanism, the number of hydroxy groups consumed in the initial and second processes can be much greater than that in the third process. This might cause the difference in the slopes in the ΔR vs. C_{APTS} plot (Fig. 10).

It now seems clear that the reaction modes of silane molecules on the silica surface depend on the nature of the silane molecule. Snyder and Ward[7] reported that the reactions of TMCS and DMDCS on the silica surface follow the processes of an initial fast reaction and a slower second reaction. For TMCS, only one reactive chlorine participates in the esterification reaction. For DMDCS, although reactivity with two adjacent surface silanols is possible as the molecule has two chlorine atoms, it was found that after one of the chlorine moieties had reacted with the hydroxy group, the second chlorine could not react with either 'normal' bound or free hydroxy groups, for energetic and geometric reasons, respectively.[2]

In this study, however, the three ethoxy groups of APTS have equivalent reactivity to that of silanols, making it possible to extend the condensation reaction and to form a coating layer of oligomers and polymers.

The quantity of γ-anilinopropyltrimethoxysilane (AnPS) modified on glass fibre has been quantitatively determined by Ikuta et al.[26] using pyrolysis-GC–FTIR. Their results suggested that the formation of a silane network through siloxane bonds is strongly dependent upon the curing time and the temperature. We suggest by analogy with our results described above, that for this reaction involving AnPS, which has three methoxy groups, the existence of several reaction processes might have been possible, causing formation of oligomerized and polymerized layers.

Conclusions

For silica gels modified with APTS at various concentrations, two types of ^{29}Si NMR spectra were measured by CP MAS and MAS methods, and CP correction factors were calculated. The integral intensities of ^{29}Si resonance lines, corrected by the CP correction factors, were found to be useful for estimation of both the concentration of APS bound per unit area and the concentrations of the $(-O)_3Si(OH)$ and $(-O)_4Si$ species in the silica gel.

From the DRIFT spectra of these same samples, it was found that the intensities of the v_{OH}^{Si} bands at 3734–3739 cm^{-1} relative to that of the SiO combination band at 1870 cm^{-1} can be used as a quantitative measure of the reactivity of APTS with the silica gel.

The concentrations of APS bound on the silica surface, determined by elemental analysis, vary with the time of removal of the APTS–silica complex from the reaction mixture and reflect the kinetics of the irreversible reaction between APTS and silica gel. This result could be explained by assuming the presence of three reaction processes, in which the reaction rate constants of the initial, second and third processes are 1.00×10^{-1}, 6.91×10^{-3} and 4.20×10^{-4} s^{-1}, respectively.

In the DRIFT spectra of these same samples, the IR bands at 3734–3739 cm^{-1} in the v_{OH}^{Si} mode region also reflect the reaction rate, and quantitative analysis of these bands provides rate constants for the three reaction processes, which closely correspond to those obtained from the time dependence of the APS concentration.

The following reaction mechanism is proposed for the three processes. In the initial reaction, the rate-determining step is

probably condensation between one of two hydroxy groups remaining uncondensed in a silane molecule and either a silica gel hydroxy group or an unreacted APTS hydroxy group. In the second reaction, unreacted APTS molecules, incorporated into the molecular gap in the first APS layer, react with a reactive hydroxy group of the silica gel, and an extended condensation between the unreacted hydroxy groups of the silane molecule bound on the surface might occur in the rate-determining step, with subsequent formation of siloxane bonds as precursors for oligomerization of the silane molecules. In the third reaction process, condensation between the unreacted hydroxy groups of the oligomers bound onto the silica gel mainly occurs and the most probable rate-determining step will then be the reaction in the growth process from oligomer to polymer.

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