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Optimization of end-capping of octadecyl-silylated silica gels by high-temperature silylation

Yoshihisa Sudo

Chemicals Inspection and Testing Institute, Division of Research and Development, 4-1-1 Higashimukojima, Sumida-ku, Tokyo 131, Japan

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Abstract

Octadecyl-silylated silicas (ODSs) end-capped by high-temperature silylation (HTS) with various organic silicon agents have been characterized by high-performance liquid chromatography of pyridine and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. All the agents exhibit end-capping effects, except for trimethylchlorosilane, and bifunctional agents being the most effective. Some of the ODSs end-capped by HTS show OH bands at 3700 and 3670 cm^{-1} on DRIFT spectra, and others show an OH band only at 3670 cm^{-1} . The ODSs without the OH band at 3700 cm^{-1} have lower adsorptivity for pyridine. The OH band area in DRIFT spectra shows a good correlation with the separation factor (α) of phenol against pyridine.

Keywords: Stationary phases, LC; End-capping; High-temperature silylation; Silylation

1. Introduction

Octadecyl-silylated silica (ODS) for high-performance liquid chromatography (HPLC) has been end-capped to delete the residual silanol groups because, on ODS, these groups interact strongly with basic solutes and cause peak tailing. In contrast, specific types of silanol groups have been reported which adsorb basic solutes and inert alkyl-bonded phases have been prepared by using silica with lower concentrations of these silanol groups. Davydov et al. [1] reported that the adsorptivity of silica must be attributed to free silanol groups. Mauss and Engelhardt [2] showed that solutes with hydroxyl groups interact with hydrogen-bonded silanol groups whereas basic solutes are adsorbed preferentially on acidic isolated silanol groups, which can be eliminated by thermal treatment of silica above 800°C. A

low amount of silanol groups was detected on octyl stationary phase prepared from silica treated thermally at 1000°C by IR spectroscopy. Köhler et al. [3,4] concluded that highly acidic isolated silanol groups cause undesired adsorption of basic solutes. They reported that full hydrolysis of silica by special techniques provided silica with a low concentration of the active silanol groups and that reversed-phase packings prepared from this silica exhibited low adsorptivity for basic solutes. However, this packing also caused peak tailing of basic solutes unless anti-tailing agents such as amines were added to the mobile phase [5]. Although it has been reported that the adsorption of basic solutes is due to metal impurities in silica [6–8], purified silica, by itself, could not provide a sufficiently inert reversed-phase packing for basic solutes [9].

In a previous study [10], I showed that ODS, with

a low amount of residual silanol groups could be prepared from silica, which was not pure and not specially pretreated, by high-temperature silylation (HTS) end-capping. Trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDS) have been widely used as agents for liquid-phase end-capping and their characteristics have been reported [11,12]. In addition, N,O-Bis(trimethylsilyl)acetamide [13,14], trimethylsilylphosphine [15] and trimethylsilylimidazole [16] have also been examined as silylating agents to improve the effect of liquid-phase end-capping. We showed that even hexamethylcyclotrisiloxane (D_3), which is a low-reactive agent in liquid-phase silylation, is an effective agent in HTS end-capping. This result suggests that the reactivity of end-capping agents in HTS end-capping is different from that in liquid-phase end-capping. We report here the characterization of ODSs end-capped by HTS with various organic silicon agents and the optimal conditions for HTS end-capping.

2. Experimental

2.1. Reagents and materials

All silicon chemicals were purchased from Shinetsu Chemicals (Tokyo, Japan). The silica gel used was Develosil 100-5 (particle size 5 μm , pore size 100 Å and surface area 300 m^2/g) from Nomura Chemicals (Seto, Japan).

2.2. Preparation of ODS

Silica was treated with conc. HCl at 100°C and silylated with octadecyltrichlorosilane by refluxing in toluene in the presence of pyridine, and the residual chloro groups were hydrolyzed. The carbon content (C%) was 16.4% and the surface coverage was 3.32 $\mu\text{mol}/\text{m}^2$. The procedure of end-capping by HTS was as follows: a 3-g amount of ODS was placed into a 30-ml glass ampoule free from cracks and strain and was dried under vacuum at 140°C for 4 h. Silylating agent (2.9 mmol) was added into the ampoule after it was cooled to about 25°C. The ampoule was cooled to about -60°C and the air in it was replaced with N_2 . The ampoule was sealed, heated for 24 h, cooled and then opened. The ODSs

were washed repeatedly with toluene and then with methanol and then dried under vacuum at 140°C for 4 h. For liquid-phase end-capping, a mixture of the ODS and HMDS in toluene was refluxed. The details of octadecylsilylation of silica and end-capping of the ODS were given previously [10].

The ODSs prepared were packed into stainless steel tubes (150×4.6 mm I.D.) by a high-pressure slurry-packing procedure.

2.3. Chromatographic measurements

The HPLC system consisted of a pump (LC-6A, Shimadzu, Kyoto, Japan), an UV detector (SPD-6A, Shimadzu), a data processor (C-R4A, Shimadzu) and an injector (Model 7125, Rheodyne, Cotati, CA, USA).

The columns prepared were tested by separating a mixture of pyridine and phenol using acetonitrile–water (3:7, v/v) as the mobile phase. The separation factor ($\alpha_{\text{ph/py}}$) of phenol (which is inert to silanol groups) against basic pyridine was measured.

2.4. Measurement of infrared spectra

Infrared spectra were obtained with a diffuse reflectance infrared Fourier transform (DRIFT) spectrometer (FTS-30, Bio-Rad, Richmond, CA, USA) purged with dry air and equipped with a deuterated triglycine sulfate (DTGS) detector. All spectra were acquired by 64 scans at a nominal resolution of 2 cm^{-1} against pure KBr as a reference. Samples were not diluted with KBr. The samples and KBr (as a reference) were dried under vacuum at 150°C for 8 h and then were measured. The reflectance data were converted to Kubelka–Munk units and band areas were integrated by using standard Bio-Rad software.

3. Results and discussion

3.1. Evaluation and preparation of ODS

Spectroscopic measurements have been used often to characterize a stationary phase. It has, however, been reported that this method does not necessarily reflect the chromatographic properties of a stationary phase [17]. In the report of Mauss and Engelhardt

[2], IR spectra did not agree with chromatographic results. Köhler et al. [3,4] reported the existence of acidic isolated silanol groups from their chromatographic results, although those silanol groups could not be detected by IR spectroscopy. Therefore, chromatography is a more useful method for evaluating inertness of reversed-phase stationary phases against basic solutes than spectroscopy. Basic compounds, such as aniline, pyridine and their derivatives, are often used as test solutes for chromatographic evaluation. I showed previously [10] that pyridine is a better test solute than aniline and its derivatives because it interacts more strongly with the residual silanol groups. Since acidic mobile phases prevent peak tailing of basic solutes [18,19], a mobile phase without a buffer solution may reveal the silanol effect. Therefore, the ODSs prepared here were also evaluated from $\alpha_{\text{ph/py}}$ values measured with the mobile phase without a buffer solution.

The C% of the ODS prepared from trichlorosilane did not decrease during HTS end-capping, whereas that of the ODS from monochlorosilane decreased [10]. Since the decrease in the C% during end-capping may result in poor reproducibility of the preparation of ODS and in chemical instability in an aqueous mobile phase, the ODS was prepared from trichlorosilane.

Table 1 shows the influence of the amount of end-capping agents and the number of end-capping runs on the characteristics of the ODSs. The change of the C% of the ODSs decreased as the amount of end-capping agents increased. Part of octadecylsilyl

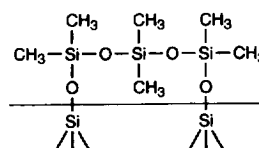


Fig. 1. Schematic representation of the crosslinkage of D_3 to the silanol groups.

groups are replaced with end-capping agents during end-capping by HTS and a higher silylation temperature promoted the present replacement [10]. This suggests that the replacement was promoted by the increase in the amount of end-capping agents as well and resulted in the decrease in the change of the C%.

A larger amount than 1.3 mmol of end-capping agent per gram of silica is not necessary because it did not improve the $\alpha_{\text{ph/py}}$ values. Since D_3 as well as 1,3-dimethoxytetramethyldisiloxane (DMTMDS) can crosslink two silanol groups, as shown in Fig. 1 [20], 1.3 mmol of the agents can end-cap 2.6 mmol of silanol groups theoretically. The silica used here has 2.4 mmol/g of silanol group, since it has 300 m^2/g of surface area and 8 $\mu\text{mol}/\text{m}^2$ of silanol group [21]. The factor, F , of trifunctional silylation is $1 < F < 2$; F is the ratio of the number of moles of silanol group reacted to the number of moles of silylating agent reacted [22]. The concentration of the residual silanol group is equal to that before the silylation (2.4 mmol per g of silica) when $F=1.5$. The amount (1.3 mmol) of the end-capping agent per g of silica is theoretically adequate to end-cap all

Table 1
Influence of the amount of end-capping agent and the number of end-capping runs on the characteristics of ODS

Packing number	End-capping agent	Number of end-capping runs	Amount of agent (mmol) ^a	$\alpha_{\text{ph/py}}$	Change in carbon content (%) ^b
1	Hexamethylcyclotrisiloxane	1	0.99	2.34	+3.6
2	Hexamethylcyclotrisiloxane	1	1.3	2.46	+2.7
3	Hexamethylcyclotrisiloxane	1	2.0	2.45	+1.4
4	1,3-Dimethoxytetramethyldisiloxane	1	1.3	3.02	+3.0
5	1,3-Dimethoxytetramethyldisiloxane	1	2.0	3.02	+1.6
6	1,3-Dimethoxytetramethyldisiloxane	2 ^c	1.3	3.65	—
7	1,3-Dimethoxytetramethyldisiloxane + HMDS	2 ^d	1.3 each	3.76	—

^a Per g of silica.

^b Expressed by $[(C_1 - C_0)/C_0] \cdot 100$, where C_0 and C_1 are the carbon contents before and after end-capping, respectively.

^c End-capping was performed twice using the same agent.

^d Sequential end-capping with these two agents.

residual silanol groups, since the concentration of the residual silanol group is less than 2.4 mmol per g of silica, if $F > 1.5$. Pfeleiderer et al. [23] reported that many silanes bonded to silica have two or three siloxane bonds when trichlorosilane is used as a silylating agent, suggesting that $F > 1.5$. The $\alpha_{\text{ph/py}}$ value of the ODS end-capped by HTS with DMTMDS, however, increased by end-capping the ODS by HTS again. These results suggest that a single run of end-capping by HTS cannot end-cap the residual silanol groups thoroughly. Methanol, a by-product that stems from the reaction with DMTMD by HTS, may partially prevent end-capping by HTS as well as steric hindrance of the octadecyl groups.

3.2. Evaluation of ODSs by HPLC

Table 2 shows the characteristics of the ODSs end-capped by HTS with various organic silicon agents and Fig. 2 shows typical chromatograms of

the mixture of pyridine and phenol on the ODSs prepared. Since the change of the C% of the ODS end-capped by HTS contains the decrease of the C% by replacement of octadecylsilyl groups with end-capping agents, the relation between the change of C% and the amount of the silanol groups end-capped is equivocal.

Although TMCS is a highly reactive silylating agent and has been extensively used as an end-capping agent, it was the least effective HTS end-capping agent among those examined in this study. The reason may be that HCl, a by-product of silylation with TMCS, cleaves a siloxane bond and forms new silanol groups [24]. N,O-Bis-(trimethylsilyl)acetamide and trimethylsilylacetamide, which are typical agents for liquid-phase silylation, were also not as effective as expected from their high reactivity. By-products may have inhibited the silylation. The thermal treatment of the original ODS without end-capping agents did not increase the $\alpha_{\text{ph/py}}$ value. HTS end-capping with

Table 2
Characteristics of ODS end-capped with various organic silicone agents

Packing number	Organic silicon agent	$\alpha_{\text{ph/py}}$	DRIFT band area ratio (OH-CH)	Index of band area ratio ^a	Wavenumber of OH band (cm ⁻¹)	Change in carbon content (%)
4	1,3-Dimethoxytetramethyldisiloxane	3.02	0.0888	16.2	3670	+3.0
6	1,3-Dimethoxytetramethyldisiloxane ^b	3.65	0.0335	6.1	3670	-
7	1,3-Dimethoxytetramethyldisiloxane+HMDS ^c	3.76	0.0538	9.8	3670	-
8	1,1,3,3-Tetramethyldisiloxane	3.01	0.123	22.4	3670	+4.4
9	Hexamethyldisilazane (HMDS)	2.99	0.113	20.6	3670	+2.3
10	Dimethoxydimethylsilane	2.86	0.116	21.2	3670	+3.0
11	Pentamethyldisiloxane	2.55	0.146	26.6	3670	+4.5
12	Hexamethylcyclotrisiloxane (D ₃)	2.48	0.141	25.7	3670	+3.3
13	Octamethylcyclotetrasiloxane (D ₄)	2.28	0.157	28.6	3670	+2.5
14	Methoxytrimethylsilane	2.23	0.105	19.1	3670, 3700	+4.2
15	N,O-Bis(trimethylsilyl)acetamide	2.13	0.109	19.9	3670, 3700	+4.2
16	N-Trimethylsilylacetamide	1.96	0.124	22.6	3670, 3700	+3.7
17	Trimethylsilanol	1.82	0.148	27.0	3670, 3700	+1.8
18	Hexamethyldisiloxane	1.80	0.145	26.4	3670, 3700	+2.0
19	Diethylmethylsilane	1.46	0.144	26.2	3670, 3700	+4.6
20	Triethylsilane	1.36	0.140	25.5	3670, 3700	+4.7
21	Hexamethyldisilane	1.37	0.179	32.6	3670, 3700	+2.5
22	Trimethylchlorosilane (TMCS)	0.812	0.231	42.1	3670	-0.86
23	Thermal treatment without agent	0.964	0.182	33.2	3700	-1.1
24	Liquid-phase end-capping with HMDS	1.994	0.406	74.0	3470, 3650	+4.6
25	ODS that was not end-capped	0.998	0.549	100	3470, 3660	-

^a Expressed by $(R_n/R_{25}) \cdot 100$, where R_{25} is the band area ratio of No. 25 packing and R_n is that of each packing.

^b End-capped twice with the same agent.

^c Sequential end-capping with two agents.



Fig. 2. Chromatogram of pyridine and phenol on the ODS prepared. A=ODS end-capped by liquid-phase silylation (packing No. 24). B=ODS end-capped by HTS (packing No. 6). Peaks: 1=pyridine; 2=phenol.

hydrosilane, siloxane or alkoxysilane, which are low-reactive silylating agents, gave larger $\alpha_{\text{ph/py}}$ values than thermal treatment without agents. These results suggest that even these agents could silylate the residual silanol groups by HTS. Conclusively, bifunctional organic silicon agents, crosslinking those, are excellent at end-capping by HTS among those examined in this study; however, HMDS, a monofunctional organic silicon agent, displayed an exceptionally high ability to end-cap. The reactivity of an organic silicon agent in HTS was not correlated with that in liquid-phase silylation.

3.3. Evaluation of ODSs by DRIFT

The OH bands observed on the DRIFT spectra of the prepared ODSs are shown in Table 2. Fig. 3 shows the typical DRIFT spectra of the ODSs and shows that the DRIFT spectra are distortion-free and sharp. Fig. 4 shows magnified spectra of the region of the silanol bands. Band assignment in IR spectra of silica gel has been summarized in Ref. [25]. The ODS without end-capping showed the OH bands at 3470 and 3660 cm^{-1} . The former is assigned to associated silanol groups and the wavenumber of the

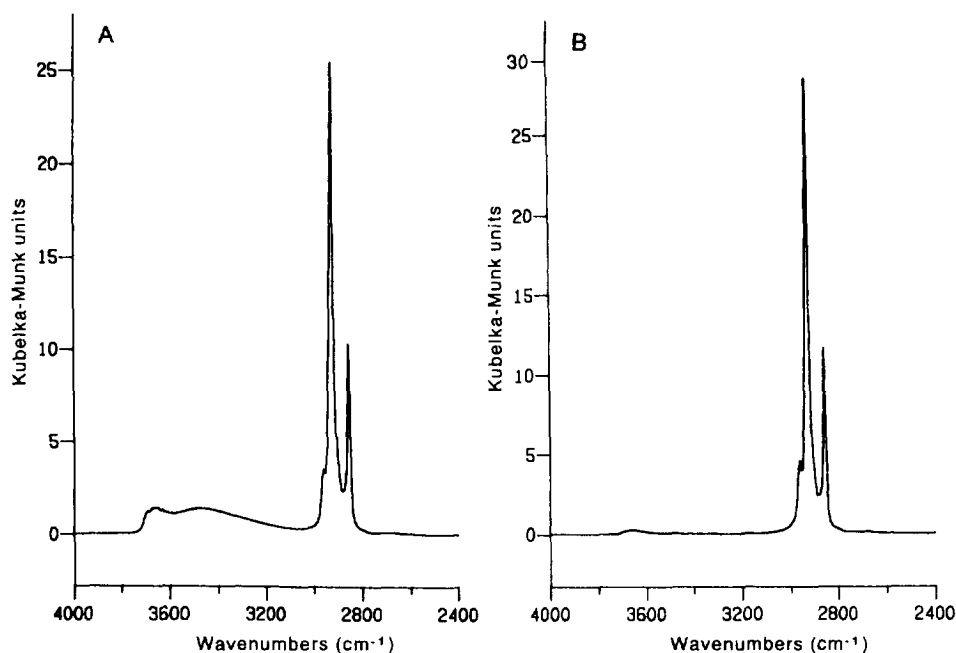


Fig. 3. DRIFT spectra of the ODSs prepared. A=ODS without endcapping (packing No. 25). B=ODS end-capped by HTS (packing No. 6).

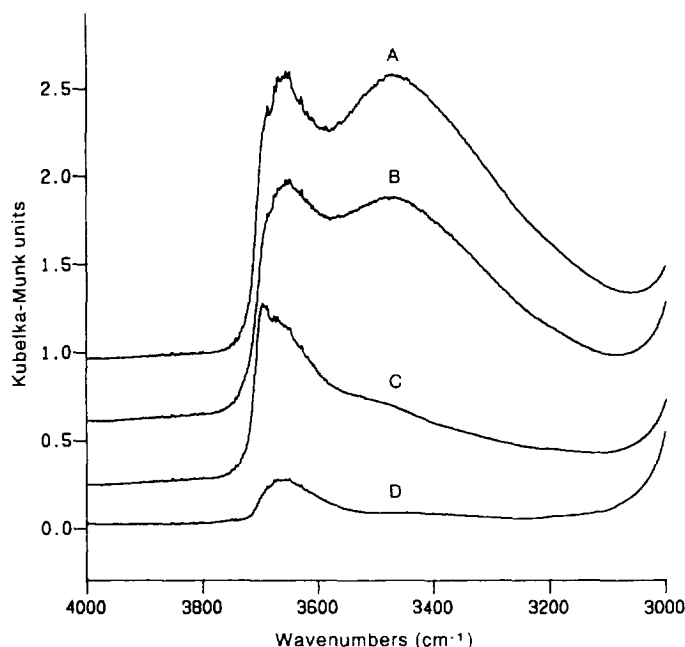


Fig. 4. Comparison of DRIFT spectra of the silanol groups on the ODSs prepared. A=ODS without end-capping (packing No. 25), B=ODS end-capped by liquid-phase silylation (packing No. 24), C=ODS end-capped by HTS with hexamethyldisilane (packing No. 19) and D=ODS end-capped twice by two HTS with DMTDS (packing No. 6).

latter almost agrees with that of silanol groups inside silica [1,26,27]. No band of the isolated silanol groups at 3750 cm^{-1} was observed. Considering that the isolated silanol groups are preferentially silylated with chlorosilane [1,2,28], this result is reasonable. End-capping of the original ODS in liquid phase slightly diminished the band area at 3470 cm^{-1} of associated silanol groups, whereas end-capping of the original ODS by HTS remarkably diminished the OH band area. In particular, the band area of associated silanol groups disappeared almost completely. As a result, the bands at 3670 and 3700 cm^{-1} became more apparent on IR spectra of packing numbers 14–21, shown in Table 2. Fig. 4C shows a typical spectrum of these ODSs. On the other hand, the OH band at 3670 cm^{-1} alone remained on IR spectra of packing numbers 4–13. Fig. 4D shows a typical spectrum of these ODSs. Boudreau and Cooper [29] observed the signal at 3690 cm^{-1} by thermal treatment of silica and concluded that it was ascribable to free and weakly hydrogen-bonded silanol groups, including some geminal silanol groups. However, others assigned the

band at about 3740 cm^{-1} to geminal silanol groups [30,31], and a NMR spectrum of alkylsilylated silica indicated that it had few geminal silanol groups [32,33].

Murthy and Leyden [34] indicated that modifiers bonded on silica can be analyzed quantitatively by estimating the ratio of the band area of modifiers to that of the siloxane on DRIFT spectra. Since concentrations of alkyl groups on all the ODSs prepared were almost the same as shown in Table 2, the concentration of the silanol groups was estimated by the ratio of the OH band area (3410 to 3800 cm^{-1}) to the CH band area (2710 to 3140 cm^{-1}). The band area ratios of the ODSs are shown in Table 2, and Fig. 5 shows the plots of the $\alpha_{\text{ph/py}}$ values against these band area ratios. The dashed line expresses the regression line for the ODSs, with a clear band at 3700 cm^{-1} , and the solid line expresses that for the ODSs, without a clear band at 3700 cm^{-1} . The band area ratio, a measure of the concentration of the silanol group, correlated quite closely with the $\alpha_{\text{ph/py}}$ values. However, the values of k' and α for the ODS of packing No. 22 may not be precise, since the peak

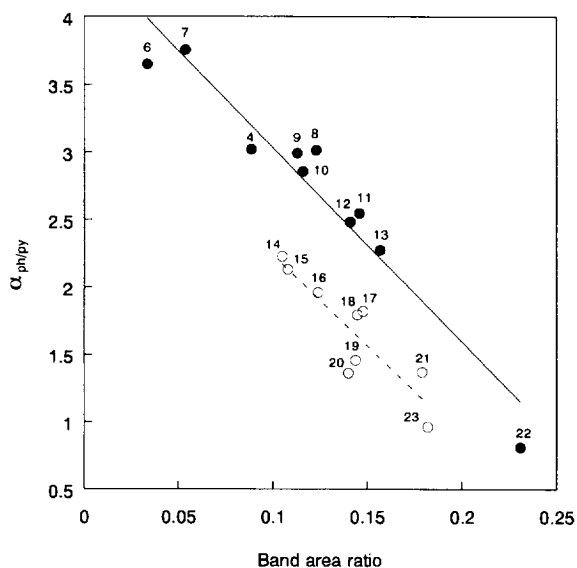


Fig. 5. Plot of the ratio (CH band area/OH band area) against the $\alpha_{\text{ph/py}}$ value. The numbers represent the packing numbers shown in Table 2. (●)=ODS without the 3700 cm^{-1} band. (○)=ODS with the 3700 cm^{-1} band.

of pyridine on it was tailing. It is noteworthy that the $\alpha_{\text{ph/py}}$ value for the ODSs with a clear band at 3700 cm^{-1} was smaller than that for the ODSs without a clear band at 3700 cm^{-1} when their band area ratios were the same. These results suggest that the silanol groups of the 3700 cm^{-1} band contribute to the adsorption of basic solutes on the ODSs. The silanol groups of the 3700 cm^{-1} band could be end-capped effectively by HTS with the bifunctional organic silicon agents that are attached to the surface of the silica, by crosslinkage. On the other hand, the silanol groups of the 3670 cm^{-1} band were difficult to end-cap, supporting the theory that some of them may be internal silanol groups. Although the solid line in Fig. 5 indicates the good correlation between the band area at 3670 cm^{-1} and the $\alpha_{\text{ph/py}}$ value, it is also assumed that the concentration of the silanol group of the 3700 cm^{-1} band, which may have been buried in the 3670 cm^{-1} band, decreased and so the $\alpha_{\text{ph/py}}$ value increased with the decrease in the concentration of the silanol group at the 3670 cm^{-1} band.

By end-capping in the liquid-phase, the signal of the associated silanol groups decreased slightly and the band area ratio did not decrease significantly,

whereas the $\alpha_{\text{ph/py}}$ value increased. Therefore, the ODS end-capped by liquid-phase silylation was out of the correlation shown in Fig. 5. On the other hand, by thermal treatment without an end-capping agent, the $\alpha_{\text{ph/py}}$ value did not increase, although the signal of the associated silanol groups and the band area ratio decreased significantly. These results suggest that the associated silanol groups do not contribute to the peak tailing of pyridine, which agrees with the information reported [2,3], if the siloxane bonding formed by dehydration of silanol groups during the thermal treatment did not rapidly hydrolyze in the mobile-phase.

4. Conclusions

The bifunctional silylating agents, which can attach to silica by crosslinkage, were effective as HTS end-capping agents. 1,3-Dimethoxytetramethyldisiloxane gave the most inert ODS among the organic silicon agents used here. The evaluation of the residual silanol groups on the ODSs by chromatography agreed well with that by DRIFT. The ODSs with a 3700 cm^{-1} band on their IR spectra interacted more strongly with pyridine than those without a clear 3700 cm^{-1} band.

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