

Reactions of HMDS, TiCl₄, ZrCl₄, and AlCl₃ with Silica As Interpreted from Low-Frequency Diffuse Reflectance Infrared Spectra

Arla Kytöki and Suvi Haukka*

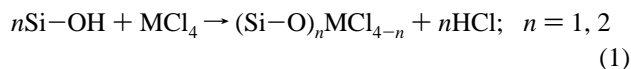
Microchemistry Ltd., P.O. Box 45, FIN-02151 Espoo, Finland

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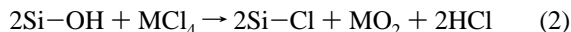
Low-frequency diffuse reflectance infrared spectra are presented for silica samples reacted with hexamethyldisilazane (HMDS), TiCl₄, ZrCl₄, and AlCl₃ vapors under different process conditions. Si–O–M bonds were observed in Ti, Zr, and Al systems at 910–930, 950, and 920–900 cm⁻¹, respectively, in the spectral window formed between the strongly absorbing SiO₂ bulk modes. Depending on the reaction temperature, at least in the case of the Ti and Zr systems the new bands were due to isolated species of type Si–O–M–Cl_x formed in reactions with OH groups or due to Si–O–M bonds between silica and crystalline metal oxide particles formed in agglomeration reactions. Thus, the appearance of Si–O–M bonds in an IR spectrum does not unambiguously reveal the interaction mechanism between metal chlorides with silica, since two types of reaction are possible. In addition to allowing the identification of adsorbed species, the low-frequency region of HMDS and AlCl₃ spectra provided information about the bonding sites: thus the band of unreacted isolated OH groups, which in the high-frequency region had shifted to the region of H-bonded groups and was no longer discernible, was clearly seen in the low-frequency region.

Introduction

The surface structures formed in the gas–solid reactions of TiCl₄, ZrCl₄, and hexamethyldisilazane (HMDS) with silica have been thoroughly studied by our group and co-workers.^{1–9} The two reaction types dominating in the interactions of TiCl₄ and ZrCl₄ are reactions with OH groups, leading to amorphous surface species and an agglomeration reaction. The OH reaction proceeds according to the following, generally accepted reaction scheme, with the formation of singly or doubly bonded species depending on whether MCl₄ reacts with one or two OH groups:

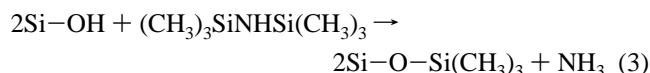


The agglomeration reaction occurring together with direct chlorination of the surface can be presented as follows:



The tendency toward agglomeration increases with the reaction temperature.^{3,8} In the reaction of TiCl₄ with silica, no agglomeration occurs at low reaction temperature of 175 °C, but reactions with OH groups according to eq 1 prevail instead. High preheat temperatures favor the formation of singly bonded surface species.² High reaction temperatures such as 550 °C for TiCl₄ and 600 °C for ZrCl₄, on the other hand, lead almost solely to the formation of agglomerates.^{3,4,8} At moderate temperatures between, both reactions occur.

HMDS reacts with isolated and terminal strongly H-bonded OH groups according to the following equation:



Whether all the isolated OH groups are silylated by HMDS is not entirely clear.⁵ Most of the strongly H-bonded groups

are in any case left available for further reactions. In the reaction of TiCl₄ after HMDS treatment, for example, the TiCl₄ reacts with strongly H-bonded groups, forming solely doubly bonded groups.²

In IR studies of these systems, the reactions described above are seen in the disappearance of bands belonging to stretching vibrations of silica hydroxyl groups in the region 4000–3000 cm⁻¹.^{2,4,5,8} It is known, however, that additional information can be obtained from the spectral window at 1000–850 cm⁻¹ in the spectrum of silica. Not only the consumption of OH groups may be seen but sometimes also the formation of surface species. For example, vibration modes of Si–O–Ti^{10–14} and Si–O–Zr¹⁵ surface species have been reported. In addition, the low-frequency region has been included in the structural characterization of gels, glasses, and mixed oxides of titania–silica and zirconia–silica.^{16–30}

In this paper we extend our earlier IR studies to the low-frequency region around 900 cm⁻¹. In the case of HMDS, TiCl₄, and ZrCl₄ reactions with silica, our interpretation is based on the same spectra that were published in refs 1, 2, 4, 5, and 8, now examined in their low-frequency region. The earlier work gives us a firm starting point for identifying the bands in the low-frequency region and thus allows us more generally to expand our knowledge about this often overlooked region.

The spectra studied were recorded from HMDS/silica, TiCl₄/silica, and ZrCl₄/silica samples prepared under various processing conditions; the main emphasis is on the TiCl₄/silica samples. The spectrum of a sample where HMDS and TiCl₄ treatments were combined and some water-treated TiCl₄/SiO₂ and ZrCl₄/SiO₂ samples were included in the study. Spectra of supported AlCl₃/SiO₂ samples, which we have not reported earlier, are presented for comparison.

Experimental Section

Supports. The two silica supports were EP-10 (Crosfield Ltd.) for HMDS, TiCl₄, and AlCl₃ reactions and Grace Davison 955 for ZrCl₄ reactions. Specific surface area for both supports was about 300 m²/g. Pore volume was 1.8 and 1.6 cm³/g and

* Corresponding author. fax int.+358 204 50 5700. tel. int.+358 204 501. e-mail Suvi.Haukka@microchem.fi. Arla.Kytokivi@microchem.fi.

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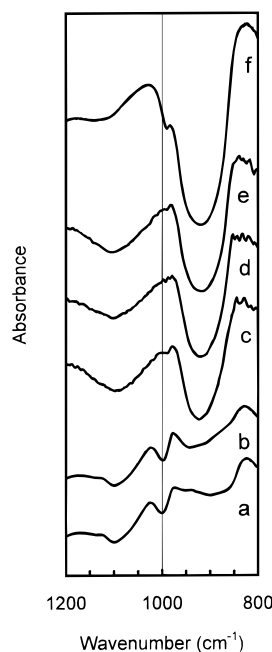


Figure 1. FTIR spectra of silica EP-10: (a) untreated, (b) preheated at 200 °C, (c) at 450 °C, (d) at 560 °C, and (e) at 750 °C. Spectrum (f) was recorded from Grace 955 silica preheated at 600 °C.

average particle size 100 and 40 μm for EP-10 and Grace 955, respectively.

Preparation of Samples. The support was preheated in air in a muffle furnace for 16 h at 200–750 °C. After this, the preheating was continued for 3 h at the same or lower temperature in a fixed-bed flow-type reactor (Microchemistry Ltd.) under pressure of 5–10 kPa in nitrogen flow. Liquid HMDS was vaporized at 50 °C and liquid TiCl_4 at room temperature. Solid ZrCl_4 and AlCl_3 were vaporized at 280–290 °C and 110–130 °C, respectively. The vapor was passed downward through the support bed at reaction temperature (175–600 °C) with nitrogen used as carrier gas. A nitrogen purge at the same temperature for at least 2 h followed the reaction. The amount of reactant always exceeded the amount needed for surface saturation. From a few samples, the chloride was removed with water vapor at the reaction temperature. In one case, HMDS reaction was followed by TiCl_4 reaction. The samples were handled and stored under nitrogen.

Characterization. A Mattson Galaxy Series 6020 or a Nicolet Impact 400D FT-IR spectrometer was used for the diffuse reflectance spectroscopy. The measurements were carried out in an accessory kept in a glovebox under nitrogen atmosphere. Spectra were obtained at 2 cm^{-1} resolution with a signal averaging 1000 scans (Mattson) or 50 scans (Nicolet). The spectra are presented in diffuse absorbance format. In the figures the spectra have been normalized using the region of overtone structure vibrations at 1950–1750 cm^{-1} , which is unaffected by thermal or modification treatments.³¹ The spectra are the same as the ones presented earlier in refs 2, 4, 5, and 8, where the OH stretching region at 4000–3000 cm^{-1} was studied. Thus, the spectra were recorded directly from the samples, without the KBr dilution commonly used for work in the low-frequency region. In the present study, the silica window and the new features appearing in the window were clear even without KBr dilution, as checked for some newly prepared, diluted samples. The dilution did, however, strengthen the intensity changes and shift the maximum absorbance at about 1025 cm^{-1} toward higher frequencies. Our discussion is therefore limited to the window region, and changes above 1000 cm^{-1} are only briefly considered.

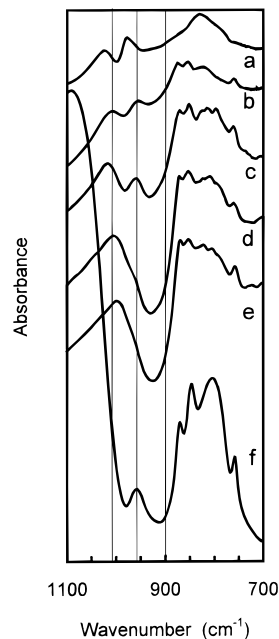


Figure 2. FTIR spectra of (a) pure 200 °C silica (EP-10) and (b–e) HMDS reacted at 200 °C with (b) 200 °C silica, (c) 300 °C silica, (d) 450 °C silica, and (e) 560 °C silica. Spectrum (f) was recorded from a diluted sample (10% in KBr) in which HMDS was reacted at 200 °C with 200 °C silica (spectrum not normalized).

The aluminum concentration of the $\text{AlCl}_3/\text{silica}$ samples was determined by X-ray fluorescence (XRF). The chloride concentration was determined by potentiometric titration with AgNO_3 after dissolving of Cl from a weighed sample into a 3.5 mol/dm^3 solution of sulfuric acid. X-ray diffraction (XRD) measurements were made with a Siemens Difract 500 instrument using Cu K α radiation. The elemental determinations of HMDS, TiCl_4 , and ZrCl_4 samples are described elsewhere.^{2,5,8}

Results

Silica Supports. Figure 1 shows the IR spectra of EP-10 silica in the 1200–800 cm^{-1} region. In the spectrum of the untreated silica (Figure 1a) bands are observed centered at about 830, 935, 975, and 1025 cm^{-1} . The bands at 975 and 935 cm^{-1} are assigned to the Si–O vibration mode of the isolated^{32–34} and H-bonded Si–OH groups,³³ respectively. The remaining bands are attributed to Si–O–Si and O–Si–O vibration modes of the silica lattice.^{32,34} When the silica is preheated to 200 °C and then to 750 °C (Figure 1b–e), a deep spectral window is formed between 850 and 975 cm^{-1} . The decreased absorption around 900 cm^{-1} and increased absorption around 1000 cm^{-1} are due to the loss of OH groups and the formation of siloxane bonds, i.e., surface Si–O–Si species.^{33,35}

Silica Grace 955 behaves similarly to EP-10 with increasing preheat temperature. The major difference is related to the band of isolated Si–OH groups at 975–984 cm^{-1} as shown for 600 °C silica in Figure 1f: the band is more clearly seen after heat treatment at high preheat temperatures, and it does not merge with the broadening band of Si–O–Si at 1020–1000 cm^{-1} .

HMDS Reactions. Figure 2 shows the low-frequency IR spectra of samples prepared by reacting silica (EP-10) preheated at 200–560 °C with HMDS at 200 °C. The number of Si–O–Si(CH_3)₃ groups (TMS groups) stays almost constant as the preheat temperature is raised, being 1.6–1.5 TMS groups/ nm^2 ,⁵ which is less than the number of isolated OH groups determined by ^1H MAS NMR. In the spectra of 200 and 300 °C silica (Figure 2b,c), an absorption band, probably due to the unreacted isolated OH groups, is seen at 960 cm^{-1} . In the spectrum of

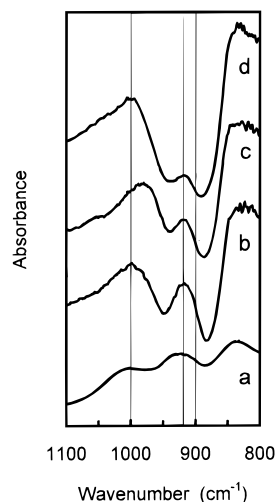


Figure 3. FTIR spectra of TiCl_4 reacted at 175 °C with (d) 750 °C silica (EP-10), (c) 560 °C silica, (b) 450 °C silica, and (a) 200 °C silica.

450 °C silica the band at 960 cm^{-1} appears as a shoulder, and in the spectrum of 560 °C silica it is hardly discernible (Figure 2d,e). In addition, a broad absorption at 950–870 cm^{-1} , due to the H-bonded OH groups, is seen in the spectrum of 200 °C silica. This absorption diminishes with increasing preheat temperature, similarly to what happens with pure silica. At frequencies lower than 900 cm^{-1} , bands attributed to methyl vibration modes of $\text{Si-O-Si}(\text{CH}_3)_3$ groups appear.^{10,12,36} These bands are more clearly seen in the KBr diluted spectra at 870, 847, and 756 cm^{-1} . Figure 2f shows the diluted spectrum of 200 °C silica reacted with HMDS as an example. Note, however, that the dilution did not affect the 960 cm^{-1} band, which is the band of interest to us. In addition, absorption increases at about 1000 cm^{-1} in the direct spectra, probably due to Si-O-Si modes of TMS groups³⁶ and the surface Si-O-Si groups, which are formed as a result of the dehydroxylation of the strongly H-bonded OH groups.

TiCl_4 Reactions. Figure 3 shows the IR spectra of samples prepared by reacting silica (EP-10) preheated at 200–750 °C with TiCl_4 at 175 °C. At this temperature the reaction takes place according to the reaction scheme (1). The low-frequency IR spectra of 450–750 °C silica show a clear increase in absorption at 920 cm^{-1} , which according to the literature¹⁰ can be attributed to Si-O-Ti surface species. The intensity of this absorption correlates with the number of bound titanium atoms, which decreases from 1.4 Ti atoms/ nm^2 on 450 °C silica to 0.7 on 750 °C silica.² The number of titanium atoms (2 Ti/ nm^2) is highest of all on 200 °C silica,² but the Si-O-Ti absorption band is less intense probably due to the absorption of unreacted isolated and H-bonded OH groups.

It has been proposed^{10,12} that the singly and doubly bonded titanium species formed in reaction 1 absorb at 1045 or 990 cm^{-1} and at 920 cm^{-1} , respectively. Whether the titanium species is singly or doubly bonded to silica can straightforwardly be determined from the Cl/Ti ratio, since the dissociation reaction with the siloxanes at 175 °C can be excluded on the basis of previous studies.² Thus, the increase in the Cl/Ti ratio from 2.5 on 200 °C silica to 3 on 750 °C silica means that half of the titanium is singly bonded and the other half doubly bonded on 200 °C silica, while only the singly bonded titanium species is present on 750 °C silica. In the case of HMDS-modified 200 °C silica reacted with TiCl_4 , the Cl/Ti ratio is 2, and thus only the doubly bonded titanium species exists.

In the IR spectrum of 200 °C silica reacted with HMDS and then with TiCl_4 (Figure 4b), a broad band is discernible centered at about 910 cm^{-1} . This band, which is solely due to the doubly

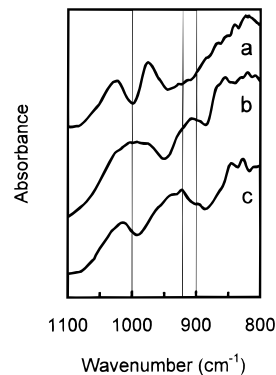


Figure 4. FTIR spectra of (a) 200 °C silica (EP-10), (b) 200 °C silica reacted with HMDS at 200 °C and then with TiCl_4 at 175 °C, and (c) 200 °C silica reacted with TiCl_4 at 175 °C and then with water vapor at 200 °C.

bonded titanium species, is somewhat shifted relative to the band at 920 cm^{-1} in the spectra of 450–750 °C silica shown in Figure 3b–d. (The increased absorption at 1000 cm^{-1} is probably due to $\text{Si-O-Si}(\text{CH}_3)_3$ groups.) On 750 °C silica, on the other hand, solely singly bonded titanium is present.² It seems therefore that, independent of the bonding mode, all titanium species bonded to silica at reaction temperature 175 °C absorb close to 920 cm^{-1} .

Figure 4c shows the low-frequency IR spectra of 200 °C silica reacted first with TiCl_4 at 175 °C and then with water vapor at 200 °C. In the low-frequency IR spectra the effect of water treatment is observed as an overall increase in absorption in the IR window relative to the spectrum of non-water-treated sample. This broad absorption band, centered at about 930 cm^{-1} , implies two things: the Si-O-Ti bonds remained intact during water treatment and the absorption was generated in the region of H-bonded OH groups. On the other hand, no clear sign of isolated OH groups reappeared during water treatment. The broad positive feature at 960–900 cm^{-1} probably also included absorption due to Ti-OH -containing species; for the earlier NMR and high-frequency IR studies have revealed the presence of Ti-OH groups in these samples.²

Figure 5 shows the IR spectra of silica samples preheated at 450, 560, and 750 °C and reacted with TiCl_4 at 450 °C, and the spectrum of 560 °C silica reacted with TiCl_4 at 550 °C. Both amorphous titanium species directly bonded to OH groups and agglomerates are present in these samples.^{3,4} On 450 and 750 °C silica, for example, 65 and 90% of titanium species, respectively, have agglomerated to crystalline TiO_2 according to reaction 2. Despite the agglomeration, however, all spectra exhibit a distinct band at about 920 cm^{-1} . In addition, a broad IR window is formed after TiCl_4 reaction because, as also seen in the high-frequency spectra,^{1,2,4} all isolated OH groups have been removed (Figure 5a–c,e).

The low-frequency IR spectra of the 560 and 450 °C silica samples reacted with TiCl_4 and water at 450 °C (Figure 5d,f) reveal the same feature as the earlier NMR and high-frequency IR studies,² that is, the reappearance of the band due to the isolated Si-OH groups at 975 cm^{-1} because the Si-Cl groups formed during agglomeration are hydrolyzed. The absorption due to Si-O-Ti seems to remain during water treatment. The IR spectra of these water-treated TiCl_4 -modified 560 and 450 °C silica samples are also similar. It seems, therefore, that besides restoring the isolated OH groups, the water treatment rehydroxylates most of the Si-O-Si groups created during pretreatment of silica from 450 °C to 560 °C.

In earlier work by Haukka et al.³ the reactions of TiCl_4 with 560 °C silica were studied at several reaction temperatures. To

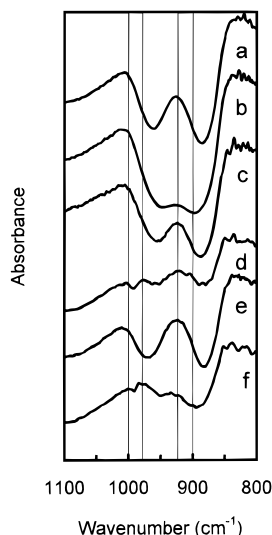


Figure 5. FTIR spectra of (a) 560 °C silica (EP-10) reacted with TiCl_4 at 550 °C, (b) 750 °C silica reacted with TiCl_4 at 450 °C, (c) 560 °C silica reacted with TiCl_4 at 450 °C, (d) 560 °C silica reacted with TiCl_4 and water vapor at 450 °C, (e) 450 °C silica reacted with TiCl_4 at 450 °C, and (f) 450 °C silica reacted with TiCl_4 and water vapor at 450 °C.

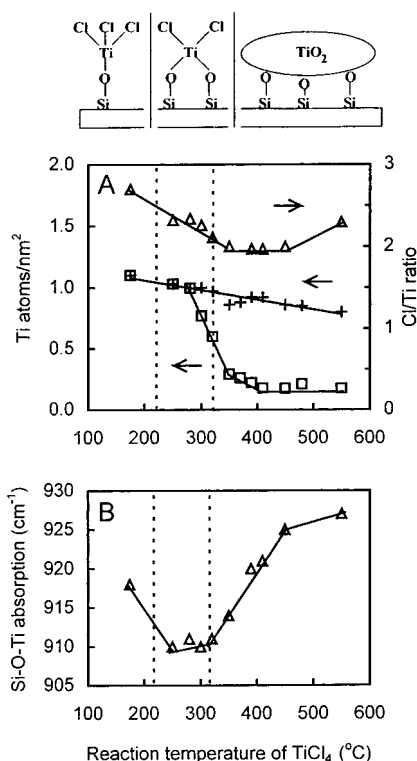


Figure 6. Reaction of TiCl_4 at 175–550 °C with 560 °C silica (EP-10): (A) (+) reacted Ti/nm^2 , (\square) etched Ti/nm^2 , (Δ) Cl/Ti ratio, and (B) position of Si–O–Ti band.

assist the reader, Figure 6a summarizes the results from these studies: the amount of titanium atoms/ nm^2 , the Cl/Ti ratios, and the amount of etchable titanium atoms/ nm^2 as a function of reaction temperature. The amount of etchable titanium atoms reveals the degree of agglomeration. Thus, all titanium can be quantitatively etched from samples containing only amorphous Ti species and the solubility decreases sharply with increasing reaction temperature. Figure 6b shows the position of the absorption band due to Si–O–Ti groups as a function of reaction temperature. When solely an amorphous singly bonded titanium species is present at 175 °C, the band is at about 920 cm^{-1} . When mainly a doubly bonded titanium species is present

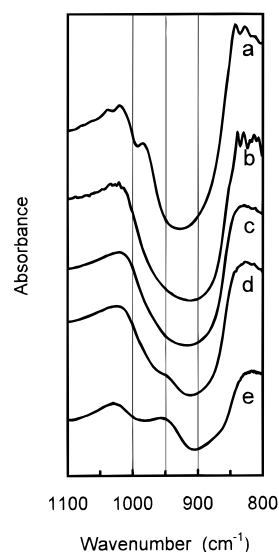


Figure 7. FTIR spectra of (a) 600 °C silica (Grace 955) and (b–e) ZrCl_4 reacted (b) at 600 °C with 600 °C silica, (c) at 450 °C with 600 °C silica, (d) at 300 °C with 600 °C silica, and (e) at 300 °C with 300 °C silica.

at 250–300 °C and no agglomeration has taken place, the band is at 910 cm^{-1} . At reaction temperature 300 °C, not all the titanium species can be etched, but the XRD spectrum does not yet show any peaks for crystalline TiO_2 , because the agglomerates are small, few in number, or somewhat amorphous in nature. At 320 °C, small peaks due to titanium dioxide appear and the amount of etchable titanium species is decreased. Further increase in the reaction temperature leads to an even smaller amount of etchable titanium species, and at the same time the IR band gradually starts moving to higher wavenumber, to 927 cm^{-1} at 550 °C, the temperature at which TiO_2 agglomerates are predominantly formed.

ZrCl_4 Reactions. Spectra of supported ZrCl_4 samples were measured after reaction of 300 °C silica (Grace 955) at 300 °C and after reactions of 600 °C silica at 300, 450, and 600 °C. Disappearance of the band of isolated Si–OH groups at about 980 cm^{-1} is clear in all spectra (Figure 7). A new band appears at about 950 cm^{-1} in the spectra of both 300 and 600 °C silica after reaction at 300 °C (Figure 7d,e). At the reaction temperature of 300 °C, the reaction 1 with OH groups is dominating,⁸ and thus the new band can be assigned to Si–O–Zr surface species.¹⁵ Higher reaction temperatures, on the other hand, lead to spectra without a distinct band in the IR window at 850–1000 cm^{-1} (Figure 7b,c). However, the window region is different from the spectrum of pure 600 °C silica (Figure 7a). It seems that the absorption increases in the region centered at about 940 cm^{-1} . The increased absorption is probably associated with the agglomerate formation typical for high reaction temperatures.⁸

The spectra of water-treated ZrCl_4 /silica samples (not shown) are similar to those of the corresponding silicas. The band of Si–OH groups at 980 cm^{-1} partly reappears in the spectra of water-treated samples, in agreement with the high-frequency spectra.⁸ The agglomeration is already effective at 300 °C, the lowest reaction temperature studied, and thus water treatment hydrolyses the Si–Cl groups of the samples. We anticipated absorption at 940–950 cm^{-1} , but it could not be distinguished as a separate band due to the disturbing absorption of the Si–OH groups.

AlCl_3 Reactions. Since we have not earlier reported results on the reactions of AlCl_3 with silica, we describe this system briefly before presenting the IR spectra. Al concentration of

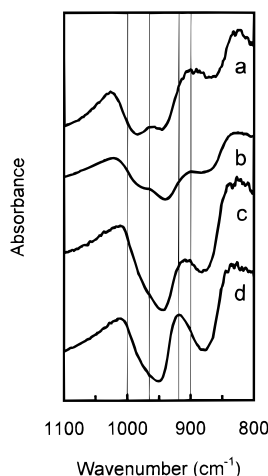


Figure 8. FTIR spectra of AlCl_3 reacted at 200 °C with silica (EP-10) preheated at (a) 200 °C, (b) 400 °C, (c) 600 °C, and (d) 750 °C.

the silica samples depended on the processing temperatures. Similarly to the TiCl_4 and ZrCl_4 systems,^{2,8} the amount of Al bound decreased with increasing reaction and preheat temperatures. The Cl/Al ratio on the surface also varied, reflecting changes in the binding mechanism. On 200 °C silica reacted at 200 °C, the Al level of 3 at/nm² was achieved with Cl/Al ratio 2. On 750 °C silica at reaction temperature 200 °C, the amount of Al decreased to 1.6 at/nm² and the Cl/Al ratio increased to 2.5. With higher reaction temperatures of 400 and 600 °C on 600 and 750 °C silica, surface densities were 0.8–1.4 Al/nm² and Cl/Al ratios 2.1–2.5. In the XRD measurements all samples appeared amorphous, in contrast to the ZrCl_4 and TiCl_4 samples which showed peaks of ZrO_2 and TiO_2 in the diffractograms after reaction at high temperatures.^{1,2,8}

Figure 8 shows the IR spectra recorded from silica (EP-10) samples after reaction of AlCl_3 at 200 °C. In the spectra of the 200 and 400 °C silica, a new band, probably due to Si–O–Al vibrations, appears at about 900 cm⁻¹ (Figure 8 a,b). It shifts to 915 cm⁻¹ on 600 °C silica (Figure 8c) and to 920 cm⁻¹ on 750 °C silica (Figure 8d). The absorption at 975 cm⁻¹ due to isolated Si–OH groups was not seen in the spectra of 600 and 750 °C silica. In the spectra of samples with lower preheat temperatures (Figure 8a,b), a small band is present at 960 cm⁻¹. Probably this is due to residual OH groups, as in HMDS samples, although the peak of isolated Si–OH groups at 3745 cm⁻¹ in the high-frequency region was not discerned on 200 and 400 °C silica supports. Only a broad band centered at 3660–3670 cm⁻¹ could be seen (not shown), and this was assigned to weakly H-bonded, inaccessible Si–OH groups.

The IR spectra recorded from samples of 400, 600, and 750 °C silica reacted with AlCl_3 at 400 °C and of 600 and 750 °C silica reacted with AlCl_3 at 600 °C were almost identical, but differed clearly from the spectra of samples reacted at 200 °C. Examples of the spectra are shown in Figure 9, together with the spectrum of 600 °C silica. The absorption in the spectrum of the pure silica (Figure 9d) is reduced in the spectra of the reacted silica (Figure 9b,c) at about 975 cm⁻¹. In the spectrum of the sample prepared on 400 °C silica (Figure 9a), however, a shoulder is observed at about 960 cm⁻¹. No intense new bands could be seen in any of the spectra, but the spectral windows at about 850–1000 cm⁻¹ are less symmetrical on the low-frequency side than they are in the spectra of pure silica supports. This nonsymmetry is due to increased absorption at about 900 cm⁻¹. In the high-frequency region (not shown), a residual peak at 3730 cm⁻¹ is observed after reactions at 400 and 600 °C with 600 and 750 °C silica. After reaction at 400 °C with 400 °C silica, a broad band due to inaccessible groups

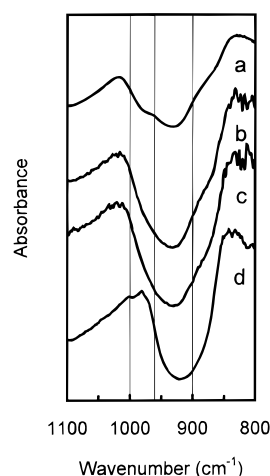


Figure 9. FTIR spectra of AlCl_3 reacted with (a) 400 °C silica (EP-10) at 400 °C, (b) 600 °C silica at 400 °C, and (c) 600 °C silica at 600 °C. Spectrum (d) was recorded from pure 600 °C silica.

is seen centered at 3680 cm⁻¹. Water treatment at the reaction temperature restored at least part of the isolated Si–OH groups after reaction at 200 °C and also after reactions at higher temperatures.

Discussion

Characterization of Silica. The spectral features recorded in the low-frequency region of the spectra of pure silica are in agreement with results in the literature,^{33,35} although the earlier DRIFTS results are reported for diluted samples.³⁵ Dehydroxylation of the surface led to formation of a deep spectral window at about 980–850 cm⁻¹ between the strongly absorbing SiO_2 bulk modes. The decreased absorption is mainly related to disappearance of the H-bonded Si–OH groups. The H-bonded groups seemed to absorb in a broad region and probably both the weakly bonded, inaccessible groups and the strongly bonded groups were included in the region. The distinct band at about 980 cm⁻¹ is generally assigned to the Si–O stretching mode of isolated OH groups.^{32–34}

Dehydroxylation of silica creates siloxane groups on the surface.³⁴ The most prominent spectral feature related to the formation of siloxanes was the increased absorption at about 1000 cm⁻¹. Especially on EP-10 silica, the increase in the absorption was so strong that the band of isolated groups became overlapped at high preheat temperatures of 560–750 °C. On Grace silica the band of isolated groups was still seen at 600 °C, which clearly indicates that the type of silica (e.g. particle size) affects the spectral features, although the behavior of the silica supports with increasing preheat temperature is considered to be similar.

HMDS Reactions. In the earlier paper dealing with HMDS reactions with silica, Haukka et al.⁵ reported contradictory results for the isolated OH groups in high-frequency IR and ¹H MAS NMR spectra. That is, the carbon determinations and measurement of isolated OH groups by ¹H NMR, indicated that about 0.5 of the isolated OH groups/nm² on 200–450 °C silica were not occupied by trimethylsilyl (TMS) groups, whereas the IR spectra in the wavenumber region 4000–3000 cm⁻¹ did not show any band due to residual isolated OH groups. Haukka et al. proposed that the band due to the unreacted isolated OH groups was not seen because the OH groups interact with the methyl groups, causing the band to shift toward lower wavenumbers.

Our present results from the low-wavenumber region 1000–850 cm⁻¹ support this proposal in showing a band due to

residual isolated OH groups at 960 cm^{-1} . In comparison with that of pure silica the band was somewhat shifted toward lower wavenumbers and the intensity was decreased. The band was more clearly seen in the spectra of HMDS-modified 200 and $300\text{ }^{\circ}\text{C}$ silica than in the spectrum of the HMDS-modified $450\text{ }^{\circ}\text{C}$ silica, where a shoulder was present, apparently because the surface Si—O—Si groups that absorb at about 1000 cm^{-1} were not formed in major quantities. The disappearance of this shoulder on $560\text{ }^{\circ}\text{C}$ silica is not related only to the formation of siloxanes, however, but also to the reactivity of practically all isolated OH groups, as indicated by the similarity in the number of isolated OH groups and bonded TMS groups.⁵ Pointing in the same direction, in the IR spectra recorded by Blitz,¹² no band due to isolated OH groups in the high-frequency region was discernible after HMDS reaction with $200\text{ }^{\circ}\text{C}$ silica. In the low-frequency spectra, however, a band was present at about 960 cm^{-1} , though this was not commented on.

TiCl₄ Reactions. The several low-frequency spectra recorded from the samples containing amorphous and/or agglomerated titanium species indicated that, independent of the surface structures formed, all titanium species absorbed near 920 cm^{-1} . The singly bonded species absorbed at 920 cm^{-1} , the agglomerated species absorbed close to 930 cm^{-1} , and the doubly bonded species present on $200\text{ }^{\circ}\text{C}$ silica after HMDS blocking and those formed at higher reaction temperatures before the agglomeration started to dominate absorbed close to 910 cm^{-1} . Our interpretation of the low-frequency spectra of the TiCl₄-modified silica samples does not entirely accord with published interpretations.

The band at 920 cm^{-1} is reported by Blitz¹² and Morrow et al.,¹⁰ but they assign it solely to doubly bonded titanium species. The singly bonded titanium species are reported to absorb at 990 ¹² or 1045 cm^{-1} ,¹⁰ and in both papers, the presence of the absorption due to these species is indicated by subtracting the corresponding silica spectrum from that of TiCl₄/silica. In Blitz's work¹² on $600\text{ }^{\circ}\text{C}$ silica after TiCl₄ reaction, when only singly bonded groups are expected, the 920 cm^{-1} band that appeared in addition to the band at 990 cm^{-1} in the difference spectrum is explained by doubly bonded titanium species formed in minor quantities in the reactions with geminal OH groups (no direct spectrum shown). In our spectra of 750 and $560\text{ }^{\circ}\text{C}$ silica reacted with TiCl₄ at $175\text{ }^{\circ}\text{C}$ a very strong absorption band at 920 cm^{-1} was observed (Figure 3), and it cannot entirely be explained by doubly bonded species in geminal groups.² We are inclined to suggest therefore that singly and doubly bonded groups absorb in the same region, just 10 cm^{-1} apart.

We can offer no explanation for the clear features in the difference spectra of other groups. We note, however, that the results of Blitz¹² and Morrow¹⁰ differ and thus reveal the difficulty of interpreting subtracted spectra, especially in regions where bulk and surface vibrations of the support overlap the possible features of new surface groups and where interaction between new groups and original groups may induce changes. A fundamental study, beyond the scope of this paper, is in order.

Voronin et al.¹³ report that water treatment of TiCl₄/silica samples results in the cleavage of Si—O—Ti bonds and a simultaneous reappearance of the Si—OH groups along with the agglomeration into TiO₂. Correspondingly, Ti—OH groups are absent from the IR spectra. In our case, however, hydrolytic cleavage of the Si—O—Ti bonds was not observed, or at least it was not dominating since the band due to Si—O—Ti groups seemed to remain unchanged in the low-frequency spectra. Also, the earlier IR and NMR studies of Haukka et al.² showed the presence of the Ti—OH groups. Earlier etching tests^{2,3} have revealed, however, that the amorphous titanium species directly bonded to the OH groups forming Si—O—Ti—Cl_x are easily

released into water solution. The contradictory results could therefore be due to the difference in the water treatment conditions. In the study of Voronin et al.,¹³ the TiCl₄/silica samples were treated with water in a closed reaction chamber, whereas in our open system the water vapor was transported through the silica bed, with the aid of flowing nitrogen, at a sufficiently high temperature, and the partial pressure of water vapor was kept at a low level. This evidently prevented the water vapor from condensing on silica, and breakage of the bonds was not favored.

The presence of a distinct band at $920\text{--}930\text{ cm}^{-1}$ in the low-frequency spectra indicates that the agglomerates formed at higher reaction temperatures of 450 and $550\text{ }^{\circ}\text{C}$ also interact with the silica surface forming Si—O—Ti bonds. To our knowledge, a similar type of bond formation has not been reported earlier. The bonds are not readily cleaved, as shown by the etching tests.^{2,3} This high stability most probably is due to the incorporation of the agglomerated titanium species into the silica matrix through a reaction with surface siloxanes. Interaction with the Si—OH groups can be excluded since these are replaced by Si—Cl groups, which absorb at essentially lower frequencies.^{36,37} The contribution of the Ti—O—Ti absorption to the band at $920\text{--}930\text{ cm}^{-1}$ does not have to be taken into account, since the TiO₂ particles in mixed oxide materials reportedly have no characteristic bands in the window region.²⁰

The clear presence of a band at $920\text{--}930\text{ cm}^{-1}$ also agrees with the proposed platelike structure of the TiO₂ particles,³ since in the platelike structure the number of Si—O—Ti bonds is maximized. In addition, the increase in the wavenumber up to 930 cm^{-1} in the spectra of samples containing almost exclusively agglomerated titanium correlates with the results obtained in the studies of mixed oxides, where a higher wavenumber of $950\text{--}935\text{ cm}^{-1}$ is reported primarily for bulk Si—O—Ti groups and to lesser extent for Si—OH groups perturbed by the presence of titanium.^{20–22,24,28} The absorption at $940\text{--}960\text{ cm}^{-1}$ in our spectra, after water treatment of amorphous TiCl₄/silica sample, we propose to be due to Ti—OH groups (no agglomerates present). This seems reasonable since the band due to Ti—OH is clearly seen in the corresponding high-frequency spectra. One may ask, therefore, whether the formation of Ti—OH groups could explain part of the absorptions present in the low-frequency spectra of mixed oxides, although we admit that mixed oxide materials clearly differ from the materials studied here.

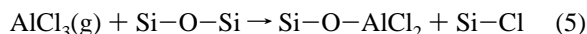
ZrCl₄ Reactions. In the ZrCl₄ system, isolated singly and doubly bonded groups are proposed to be the main species on the surface of silica after reaction at $300\text{ }^{\circ}\text{C}$.⁸ The low-frequency spectra of our supported samples are consistent with this. The band at about 980 cm^{-1} on pure silica disappeared, analogously to the change in the high-frequency spectra, and as suggested in the literature,¹⁵ and analogously to the TiCl₄ system, the new band at about 950 cm^{-1} could be attributed to the formation of surface Si—O—Zr linkages. In the studies of mixed oxides, bulk Si—O—Zr linkages are reported to occur at $975\text{--}980\text{ cm}^{-1}$ ^{17,18,25,29} or 1063 cm^{-1} ²⁷ in IR spectra.

The distinct band belonging to surface species originating from OH reactions could no longer be seen in the spectra of supported ZrCl₄ samples at reaction temperatures of 450 and $600\text{ }^{\circ}\text{C}$. The absorption seemed to be increased, however, at about the same position as at reaction temperature $300\text{ }^{\circ}\text{C}$. On the basis of the earlier work on the ZrCl₄ system,⁸ we cannot assign this absorption to isolated surface species, at least at reaction temperature $600\text{ }^{\circ}\text{C}$, and we connect it instead to the formation of ZrO₂ agglomerates. Thus, we arrive at the same conclusion as for the TiCl₄ system. The increased absorption

is proposed to be connected with vibration modes of Si—O—Zr linkages which are formed between the silica surface and agglomerates. Indeed, literature on the bulk ZrO₂ shows that the pure oxide cannot be expected to have characteristic bands in the area.^{25,29} For the mixed oxides, SiO₂—ZrO₂, a band at 740 cm⁻¹¹⁷ or 600 cm⁻¹¹⁸ is reported to originate from Zr-rich domains.

Because of the reappearance of the Si—OH band at 970–980 cm⁻¹ and its interfering effect, the stability of Si—O—Zr bonds is not so evident in water-treated samples of the ZrCl₄ system at reaction temperature 300 °C as in the TiCl₄ system at reaction temperature of 175 °C. Reaction at 300 °C, namely, leads to agglomeration and the formation of Si—Cl groups, which are then hydrolyzed in the water treatment.⁸ The high-frequency IR and ¹H MAS NMR spectra recorded after water treatment show that not all of the Si—OH groups reappear, however, and that Zr—OH groups are formed on the surface.⁸ This clearly implies that the Si—O—Zr bonds are not cleaved in major quantities in the water treatment.

AlCl₃/SiO₂. Literature reports suggest that AlCl₃ reacts with OH groups forming Si—O—Al—Cl₂ or (Si—O)₂Al—Cl species^{38–46} even at reaction temperatures of 500–600 °C.^{39,46} Additionally, dimeric Al₂Cl₄⁴¹ or Al₂Cl₅⁴⁶ structures on the surface have been proposed to form in reactions at 150 and 200 °C since AlCl₃ exists mainly as a dimer, Al₂Cl₆, in gas phase at these temperatures. Also, an etching reaction leading to elimination of SiCl₄, as shown in reaction scheme (4), is reported to occur at 400–450 °C.⁴⁷ The reaction can be expected to proceed through chlorination of the silica surface and through cleavage of the siloxane bonds of the framework silica in the presence of sufficient excess of the AlCl₃ reagent. In the first stage, the reaction with siloxane groups is then a dissociation reaction according to reaction 5. Thus, after the dissociation reaction, water treatment would release Si—OH groups.



To the list of possible reaction mechanisms, we can add the agglomeration reactions without water treatment² and during water treatment.¹³ Both reactions would lead to the reappearance of Si—OH groups during water treatment, as was observed in here and in earlier work by Peri³⁹ and Peglar et al.⁴¹

Similarly to the TiCl₄ and ZrCl₄ systems, but without support for this assignment in the literature, we tentatively assign the distinct band occurring at 900–920 cm⁻¹ in all spectra at 200 °C to Si—O—Al bonds. The shift in wavenumber with preheat temperature, together with the changing Cl/Al ratio, would then imply different surface species dominating at each preheat temperature. No distinct band was observed in the spectral window at reaction temperatures of 400 and 600 °C, but the increased absorption at about 900 cm⁻¹ might be related to isolated species formed in the OH reaction or in the dissociative reaction, though in principle it might also be related to XRD amorphous agglomerates. The observation of Si—O—Al bond formation and reappearance of part of the Si—OH groups, together with elemental analyses, is not enough to resolve the binding mechanism. We can say, however, that our results do not fully support the view presented in the literature for AlCl₃. At least, none of the earlier studies explain all the findings we have made over a wide range of processing temperatures.

Finally, we need to consider the band at 960 cm⁻¹ found in the spectra of the two lowest preheat temperatures after AlCl₃ reaction at 200 °C. This was assigned to isolated OH groups left unreacted. The shift from 980 cm⁻¹ was then a result of

the interaction between surface species and residual OH groups. This interaction would also explain the absence of an absorption for isolated groups in the high-frequency region. Namely, here, as also in the HMDS system, the absorption of the residual OH groups was shifted to the region about 3660 cm⁻¹, where absorption due to inaccessible weakly H-bonded OH dominates. In the low-frequency region the weakly H-bonded OH groups evidently did not disturb the spectra and the shift of the band could be seen. By contrast, in the TiCl₄ system after reaction at 175 °C with 200–750 °C silica,² in the ZrCl₄ system after reaction at 300 °C on 600 °C silica,⁸ and in the AlCl₃ system after reactions at 400 and 600 °C on 600 and 750 °C silica, a band due to residual isolated OH groups was seen in the high-frequency region at 3748–3730 cm⁻¹. In the low-frequency region absorption due to surface Si—O—Si was probably overlapping the 980 cm⁻¹ band. In the case of ZrCl₄, also the Si—O—Zr vibrations at about 950 cm⁻¹ probably interfered. Thus, the information obtainable about the unreacted isolated OH groups in the low-frequency spectra varies with the system in question. In a similar way, Si—O—metal bonds in these systems are seen either as a distinct band or only as increased absorption. How the bands appear seems to depend on where the absorption is located in the window region.

Summary. Study was made of the low-frequency diffuse reflectance IR spectra of silica samples reacted with HMDS, TiCl₄, ZrCl₄, and AlCl₃ vapor under different processing conditions. The spectra of some water-treated samples were investigated as well. The results showed that complementary information to that provided by high-frequency IR spectra can be obtained from IR bands in the spectral window formed between the strongly absorbing SiO₂ bulk modes at about 850 and 1000 cm⁻¹. New information can be obtained both on bonding sites and on the surface species formed in the reactions. First, the region may reveal the presence of unreacted isolated OH groups in situations where the band in the high-frequency spectrum is shifted to the region where H-bonded OH groups absorb. This was the case in reactions of HMDS and AlCl₃ with silica preheated at low temperatures. Second, the formation of Si—O—metal (Ti, Zr, Al) bonds may be observed. Increased absorptions were found at 910–930, 950–940, and 920–900 cm⁻¹, in Ti, Zr, and Al systems, respectively. Due to narrowness of the spectral window, however, only vibrations located in the middle of the spectral window are observed as distinct bands. Vibrations in side regions of the window are disturbed by the bulk and surface Si—O—Si vibrations and Si—O stretching vibration of isolated Si—OH groups.

Moreover, depending on the reaction temperature and reaction mechanism as identified in earlier studies of TiCl₄ and ZrCl₄ systems, bands due to isolated species of type Si—O—M—Cl_x formed in reactions with OH groups occur at about the same frequency as bands due to Si—O—M bonds between silica and crystalline TiO₂ and ZrO₂ particles formed in an agglomeration reaction. A detailed analysis of the TiCl₄ system showed, however, that the frequency of absorption changes from 910 cm⁻¹ to 920 cm⁻¹ and further to 930 cm⁻¹ on going from doubly to singly bonded groups and to agglomerates. The singly and doubly bonded groups have earlier been proposed to absorb at clearly distinct frequencies. In the AlCl₃ system, no definitive conclusion about the reaction route or surface species formed could be made solely on the basis of elemental analysis and IR spectra because the proposed formation of Si—O—Al bond does not reveal the interaction mechanism.

The Si—O—Ti bonds were preserved in the water treatment. In the TiCl₄ system, Ti—OH groups were proposed to occur at 940–960 cm⁻¹. On the whole, however, the spectra are more

difficult to interpret because the several types of OH groups absorb in a broad region in the window.

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