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Aminosilane as a coupling agent for cyclopentadienyl ligands on silica

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Abstract

Aminosilane has been used as a coupling agent for cyclopentadienyl (Cp) ligands on silica surfaces. First the silica surface was functionalized with aminopropyldimethylethoxysilane (APDMES) by using saturated gas–solid reactions. Secondly two different (tetramethylcyclopentadienyl)chlorosilanes, $Me_2Si(C_5Me_4H)Cl$ and $MeHSi(C_5Me_4H)Cl$, were immobilised on the APDMES-functionalized silica by utilising *n*-BuLi (*n*-butyllithium). The amine groups react with *n*-BuLi by producing lithiated amine groups. Furthermore, the lithiated amine reacts with chloride of the silane and a chemical bond between nitrogen and silicon of the silane is formed. These stepwise prepared surfaces were characterised with ^{1}H-, ^{13}C- and ^{29}Si- solid state NMR and FTIR spectroscopy.

Keywords: Silica; Silane; Cyclopentadienyl; Amine; FTIR spectroscopy; Nuclear magnetic resonance

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1. Introduction

In the last few years there has been considerable interest in the heterogenization of homogeneous transition metal catalysts. The immobilisation of metal catalysts on inorganic or organic supports can be accomplished by using suitable anchoring ligands. For this purpose one suitable ligand is the cyclopentadienyl (Cp) group which is a commonly used group in many homogeneous catalysts, e.g. metallocenes [1]. Heterogenization of Cp groups has usually been done by using different silanes containing Cp groups [2–7]. In our method the silica surface was first functionalized with aminosilanes using gas-phase reactions and the Cp group was introduced in the second step. Liquid-phase reactions of aminosilanes with silica have been studied at least for 20 years in many research groups [8]. According to our knowledge none has modified the silica with aminosilanes in the gas phase.

We have concentrated, in our studies, on preparing a Cp-modified silica surface, on which suitable homogeneous transition metal catalysts can be immobilised. In our earlier report [9] we introduced a method for immobilising tetramethylcyclopentadienylsilanes on APTES (aminopropyltriethoxysilane)-modified silica. In that study we faced some obstacles with unreacted ethoxy groups which disturbed the surface modification in the next step. These problems have been solved in this report, by using APDMES (aminopropyldimethylethoxysilane) for silica modification. This aminosilane has only one ethoxy group that reacts with the silica surface and no unreacted ethoxy groups remain.

In the first stage the silica surface was modified with APDMES using a new ALCVD (atomic layer chemical vapour deposition) method utilising saturated gas–solid reactions [10–13]. In the second step two different (cyclopentadienyl)chlorosilanes, $Me_2Si(C_5Me_4H)Cl$ and $MeHSi(C_5Me_4H)Cl$, were immobilised on the surface using liquid-phase reactions. The ALCVD method was found convenient for modification of the silica, since total saturation of the surface with APDMES molecules takes place. An alternative method, impregnation of APDMES on the silica from the liquid phase, rarely results in total saturation of the surface [14].

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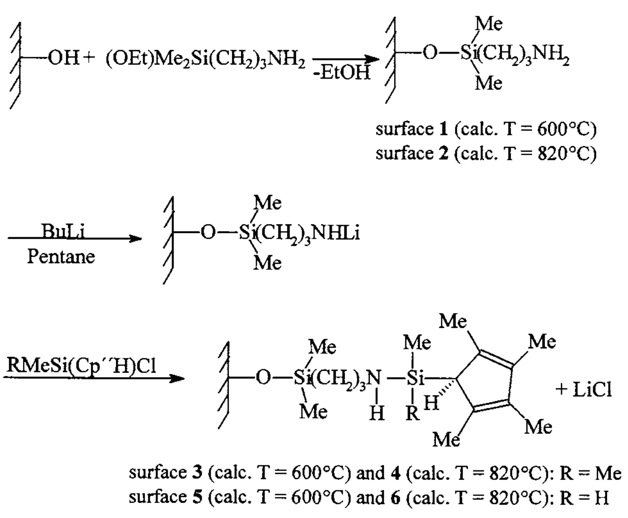
2. Results and discussion

2.1. Modification of silica with aminopropyldimethylethoxysilane

Pretreatment of silica was performed by calcination either at 600 or 820°C. The heat treatment of silica in air at 600°C leads to a material that contains ca. 1.8–1.9 OH groups nm^{-2} [15,16]. About 80% of them are isolated OH groups and the rest hydrogen bonded OH groups [15,16]. The calcinated silica was modified with APDMES in an ALCVD reactor, utilising saturated gas–solid reactions (Scheme 1). The nitrogen analysis after modification corresponds to ca. 1.5 N atoms (or APDMES molecules) nm^{-2} of SiO_2 (surface **1**). The heat treatment of silica at 820°C leads to material that contains ca. 1.1 OH groups nm^{-2} and all of them are isolated [15,16]. Modification of this pretreated silica with APDMES gives a material containing ca. 1.0 N atom (or APDMES molecule) nm^{-2} of silica (surface **2**).



Scheme 1. Modification of the silica surface with APDMES and further immobilisation of $Me_2Si(C_5Me_4H)Cl$ and $MeHSi(C_5Me_4H)Cl$ on it by utilising *n*-BuLi.

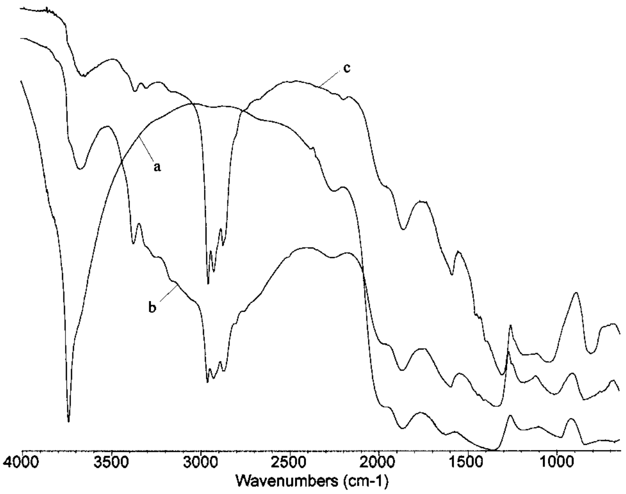


Fig. 1. IR spectra of (a) heat treated (600°C) neat silica, (b) APDMES modified a, surface **1** and (c) b after *n*-BuLi treatment.

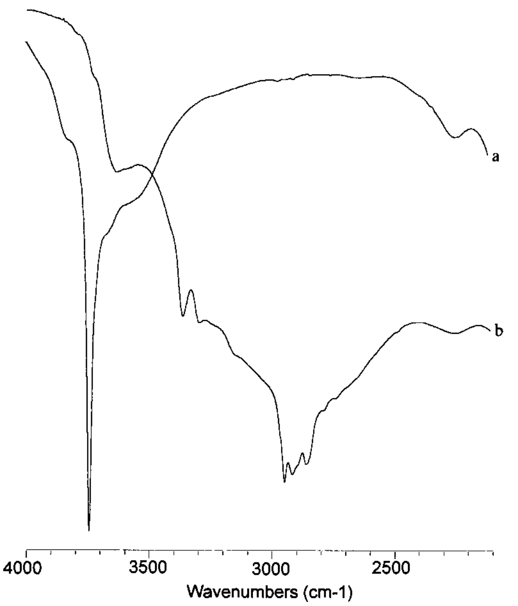


Fig. 2. IR spectra of (a) heat treated (820°C) neat silica and (b) APDMES modified a, surface **2**.

In the IR spectra of surfaces **1** and **2** (Figs. 1 and 2) the disappearance of absorption at 3741 cm^{-1} indicates that most of the isolated Si–OH groups in heat-treated silica are bonded to aminosilane via Si–O–Si bridges. The less intense absorption at 3650 cm^{-1} in the IR spectra of surfaces **1** and **2** represents internal and hydrogen bonded Si–OH groups that cannot interact with the alkoxysilane. In the IR spectrum of neat APDMES the amine stretching absorptions occur at 3380, 3301 and bending at 1618 cm^{-1}. The DRIFT (diffuse reflectance infrared fourier transform) spectrum of APDMES-modified silica reveals amino stretching absorptions at 3369, 3302 and bending at 1591 cm^{-1}. The hydrocarbon frequencies of the APDMES-modified silica are at their normal positions.

The CP/MAS ^{13}C-NMR spectrum of APDMES modified silica (Fig. 3a and b) shows four signals: three signals of propyl spacer ($H_2NCH_2(1)CH_2(2)CH_2(3)Si$) at 45 (C1), 27 (C2) and 14 (C3) ppm and the signal of methyl groups bound to silane at -3 ppm [8,14]. In the case of surface **2** there are furthermore some ethoxy groups (OCH_2CH_3) bound on the surface. The reaction mechanism of the strained siloxanes of silica with alkoxysilanes has been confirmed by Blumel [17]. The signal of the OCH_2 group can be found at 59 ppm but the signal of the methyl group is at the same chemical shift as the (C2) signal of the propyl spacer. In the ^{29}Si spectra of surfaces **1** and **2** the resonance of silica can be seen at − 110 ppm and the signal of APDMES at 13 ppm (Fig. 4a and b).

2.2. Immobilisation of (tetramethylcyclopentadienyl)methylchlorosilanes on APDMES-functionalized silica

Immobilization of (tetramethylcyclopentadienyl) methylchlorosilanes on APDMES-modified silica was carried out by utilising *n*-BuLi (*n*-butyllithium). The reaction of the amine group on the modified silica surface with *n*-BuLi in pentane produces a lithiated amine group, which reacts further with a chloride of the silane and a chemical bond between nitrogen and silicon of the silane as well as lithium chloride (LiCl) as a by-product, are formed (Scheme 1). The tailored surfaces were analysed with solid state CP/MAS-NMR and IR spectroscopy.

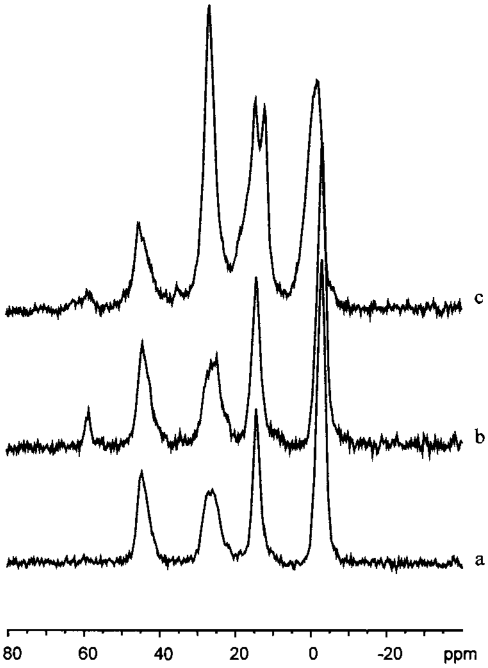


Fig. 3. CP/MAS ^{13}C-NMR spectra of (a) APDMES modified silica (silica calcinated at 600°C), surface **1**, (b) APDMES modified silica (silica calcinated at 820°C), surface **2**, (c) a after *n*-BuLi treatment.

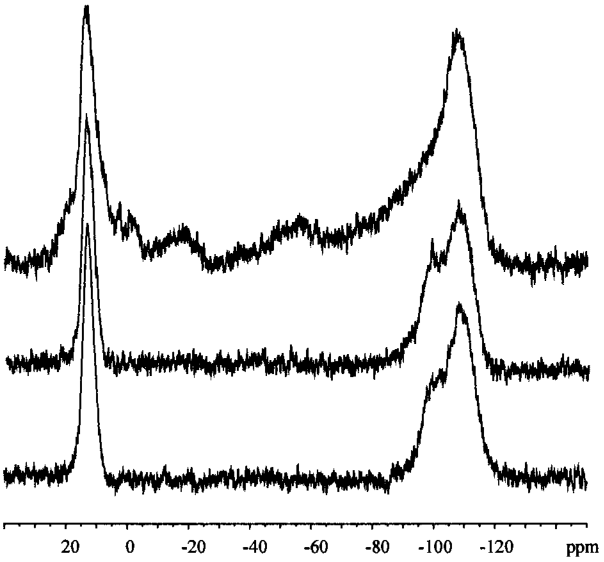


Fig. 4. CP/MAS ^{29}Si-NMR spectra of (a) APDMES modified silica (silica calcinated at 600°C), surface **1**, (b) APDMES modified silica (silica calcinated at 820°C), surface **2**, (c) a after *n*-BuLi treatment.

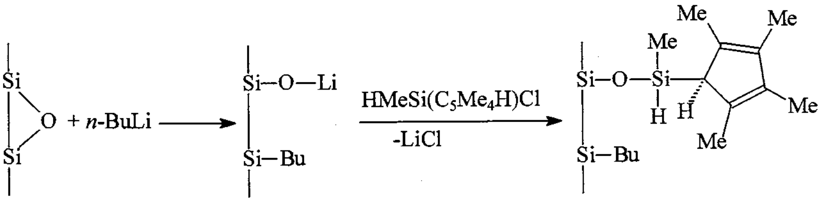
2.2.1. Butyllithium treatment of APDMES-modified silica

Butyllithium treatment of APDMES-modified silica (both surface **1** and **2**) seems to have an effect besides on the amine groups also on the siloxane bridges of the silica. Butyllithium induces to some extent opening of the siloxane bridges and results in the binding of lithium (silica–O–Li) and butyl (silica–Bu) groups on the surface (Scheme 2). This phenomenon can be observed in ^{13}C-NMR (Fig. 3(c)). After *n*-BuLi treatment in the ^{13}C-NMR spectrum, a new signal at 11.9 ppm is observed and furthermore, the intensity of the signal at about 26–27 ppm has increased. In the ^{29}Si-NMR spectrum some new broad resonances at about − 15 ppm and − 60 ppm can be seen (Fig. 4(c)). These resonances can be assigned to surface silicons that have reacted with butyl and lithium groups. Bade et al. [18] has also suggested that the siloxane bridges of silica can react with butyllithium.

2.2.2. Immobilisation of $Me_2Si(C_5Me_4H)Cl$ (surfaces **3** and **4**)

Immobilization of $Me_2Si(C_5Me_4H)Cl$ has been studied both on surface **1** (silica calcinated at 600°C before modification with APDMES, product: surface **3**) and on surface **2** (calcinated at 820°C, product: surface **4**). $Me_2Si(C_5Me_4H)Cl$ was used in light excess (1.5-fold). Immobilisation seems to succeed on both surfaces and the NMR spectra of the new surfaces **3** and **4**, obtained show no significant difference between these two materials. The only differences are in the intensities of the signals due to the APDMES and $Me_2Si(C_5Me_4H)Cl$ molecules attached on the surface. In the case of surface **1** every amine group has not reacted with $Me_2Si(C_5Me_4H)Cl$ molecule. The reason for this probably derives from the high surface density of the APDMES molecules. The amine groups are probably too close to each other so that the bulky $Me_2Si(C_5Me_4H)Cl$ molecules cannot reach each amine group. In the case of surface **2** the APDMES molecules are more easily achieved and the amine groups are better saturated with $Me_2Si(C_5Me_4H)Cl$ molecules.

The ^{13}C-NMR spectra of surfaces **3** and **4** show that the immobilisations have succeeded (Fig. 5). The two



Scheme 2. Reaction of *n*-BuLi with reactive siloxane bridge of silica results binding of butyl and lithium groups on the surface. Further, the surface lithium group can react with MeHSi(C_5Me_4H)Cl.

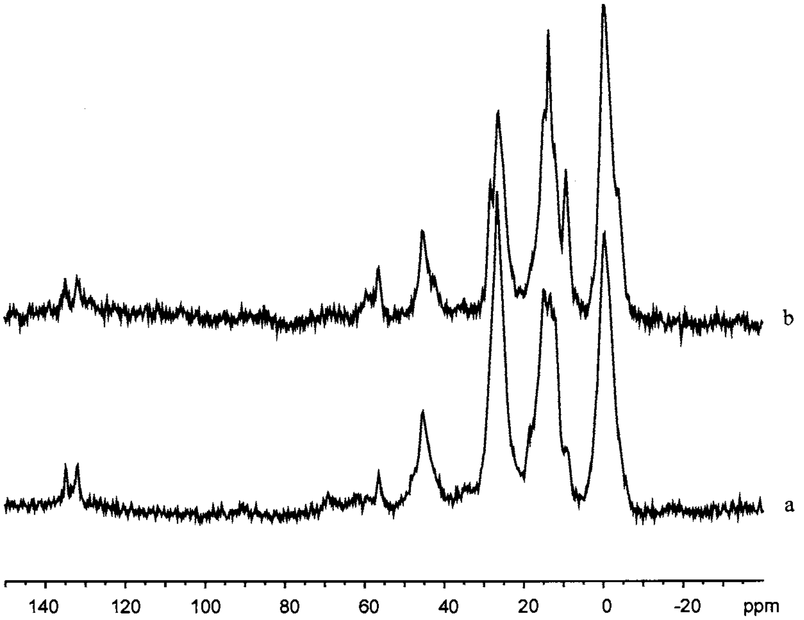


Fig. 5. CP/MAS ^{13}C-NMR spectra of (a) surface **3**, APDMES-modified silica after immobilisation of $Me_2Si(C_5Me_4H)Cl$ (silica calcinated at 600°C), (b) surface **4**, APDMES-modified silica after immobilisation of $Me_2Si(C_5Me_4H)Cl$ (silica calcinated at 820°C).

signals of the quaternary carbon atoms of the double bonds of the (C_5Me_4H)-ring at 132 and 135 ppm give the best evidence of the immobilisations. These resonances are the only signals in this area. A new signal at 56 ppm is assigned to aliphatic methine carbon (CH) of the (C_5Me_4H)-ring. Furthermore two signals of the methyl groups of the ring can be found at about 9 and 13 ppm.

The ^{29}Si-NMR spectrum of the surfaces **3** and **4** shows only three distinct signals, as expected: the resonances of silica at -110 ppm, APDMES at 12.7 ppm and immobilised the $Me_2Si(C_5Me_4H)Cl$ at 1.6 ppm (Fig. 6). Also the broad resonances at about -15 ppm and -60 ppm caused by the *n*-BuLi treatment can still be observed.

There are only a few new bands in the IR spectra of surfaces **3** and **4** because the silica carrier obscures most of the bands (Fig. 7). One new band is found at about 3413 cm^{-1} and can be assigned to the N–H stretching of the secondary amine. Another new band is a C=C stretching band of the Cp ring at 1630 cm^{-1}.

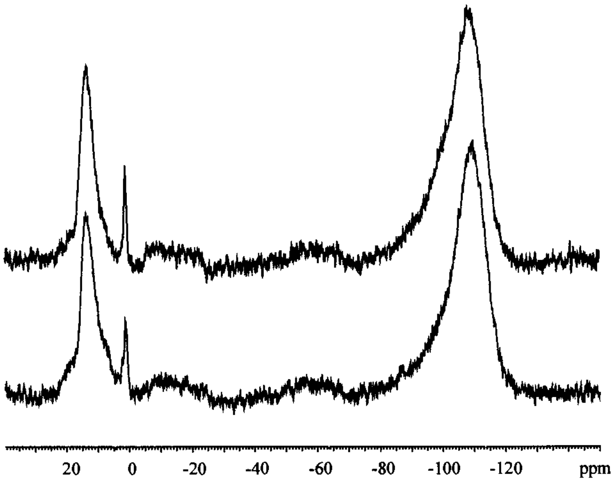


Fig. 6. CP/MAS ^{29}Si-NMR spectra of (a) surface **3**, APDMES-modified silica after immobilisation of $Me_2Si(C_5Me_4H)Cl$ (silica calcinated at 600°C), (b) surface **4**, APDMES-modified silica after immobilisation of $Me_2Si(C_5Me_4H)Cl$ (silica calcinated at 820°C).

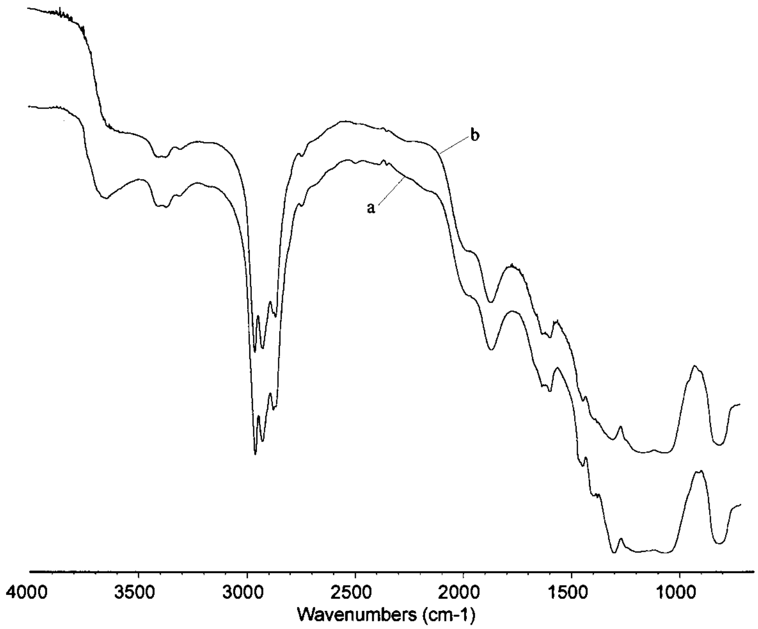


Fig. 7. IR spectra of (a) surface **3**, APDMES-modified silica after immobilisation of $Me_2Si(C_5Me_4H)Cl$ (silica calcinated at 600°C), (b) surface **4**, APDMES-modified silica after immobilisation of $Me_2Si(C_5Me_4H)Cl$ (silica calcinated at 820°C).

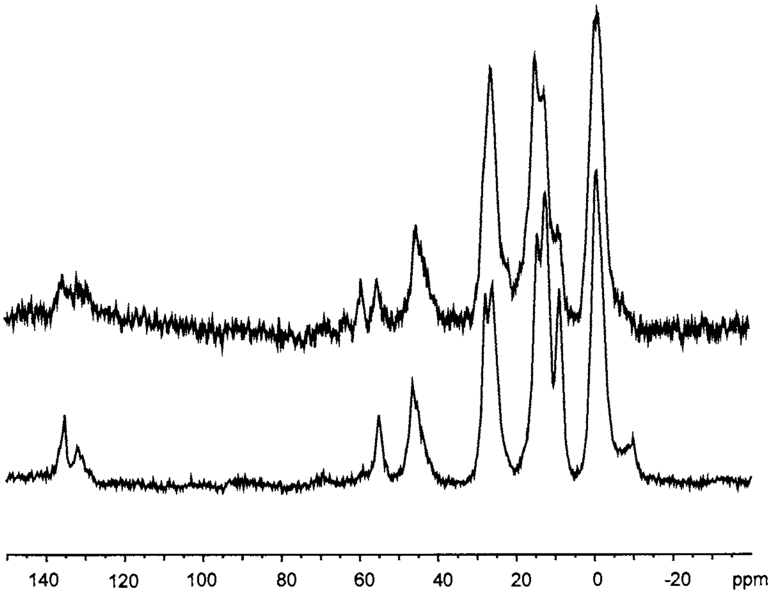


Fig. 8. CP/MAS ^{13}C-NMR spectra of (a) surface **5**, APDMES-modified silica after immobilisation of $MeHSi(C_5Me_4H)Cl$ (silica calcinated at 600°C), (b) surface **6**, APDMES-modified silica after immobilisation of $MeHSi(C_5Me_4H)Cl$ (silica calcinated at 820°C).

2.2.3. *Immobilisation of $MeHSi(C_5Me_4H)Cl$ (surfaces **5** and **6**)*

The immobilisation of $MeHSi(C_5Me_4H)Cl$ has also been investigated both on surface **1** (silica calcinated at 600°C before modification with APDMES, product: surface **5**) and on surface **2** (calcinated at 820°C, product: surface **6**). $MeHSi(C_5Me_4H)Cl$ was used in light excess (1.5-fold). By comparing ^{13}C-NMR spectra of these two prepared materials (surface **5** and **6**) some differences can be found in the area of 130 ppm where the signals of the quaternary carbon atoms of the double bonds of the ring are observed (Fig. 8). For surface **5** two signals can be found in this area, as expected, but in the case of surface **6** there are actually broad resonances. The other parts of the ^{13}C spectra are quite similar.

The ^{29}Si-NMR spectrum of surface **5** (Fig. 9(a)) shows the same silica and APDMES resonances as for surfaces **3** and **4** and the signal of the immobilised $MeHSi(C_5Me_4H)Cl$ can be found at -9.3 ppm. More-

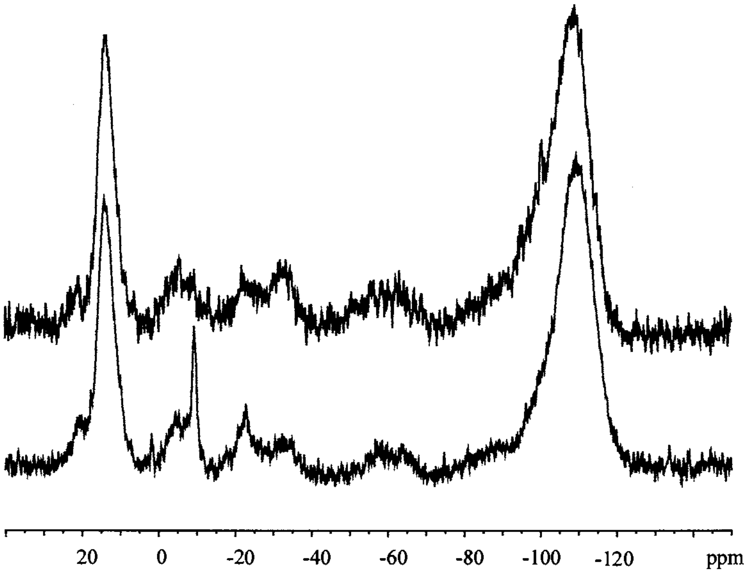


Fig. 9. CP/MAS ^{29}Si-NMR spectra of (a) surface **5**, APDMES-modified silica after immobilisation of MeHSi(C_5Me_4H)Cl (silica calcinated at 600°C), (b) surface **6**, APDMES-modified silica after immobilisation of MeHSi(C_5Me_4H)Cl (silica calcinated at 820°C).

over, there are the broad resonances between -15 ppm and -60 ppm caused by the *n*-BuLi treatment and a signal at -22 ppm. The -22 ppm signal can be assigned to MeHSi(C_5Me_4H)Cl molecules bound directly to the surface after reaction with lithium group of the surface (Scheme 2). In the ^{29}Si-NMR spectrum of surface **6** (Fig. 9(b)) no distinct signal at -9 ppm due to MeHSi(C_5Me_4H)Cl bound to the amine groups is found but the same broad resonances observed in the case of surface **5** can be seen.

The combined NMR results indicate that in the case of MeHSi(C_5Me_4H)Cl the calcination temperature influences the structure of the resulting surface. In the case of surface **2** due to the higher calcination temperature the APDMES surface coverage is lower and there are more space between the aminopropyl molecules when compared with surface **1**, and therefore the MeHSi-(C_5Me_4H)Cl molecules can react more easily with the lithium groups (silica–O–Li) on surface **2**. From the above ^{29}Si-NMR observation we can conclude that MeHSi-(C_5Me_4H)Cl molecules react preferably with lithium groups on the surface than with the lithiated amine groups.

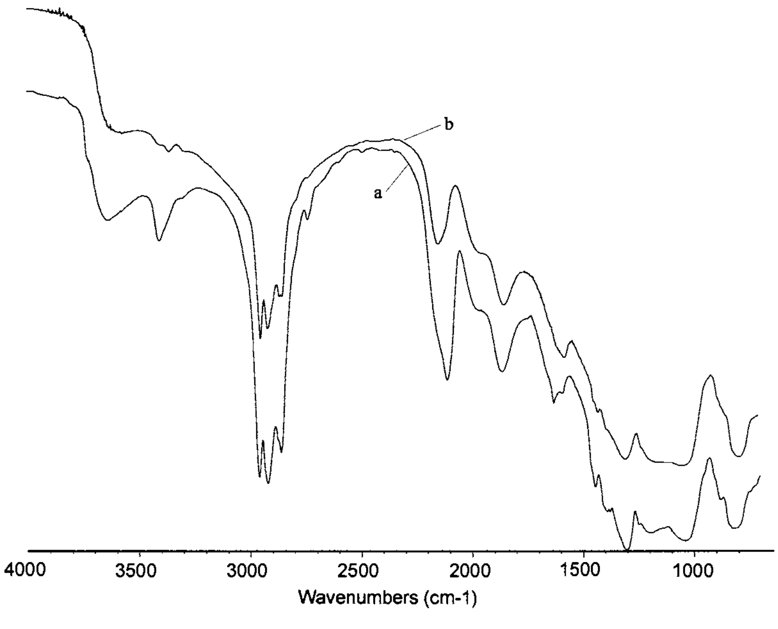


Fig. 10. IR spectra of (a) surface **5**, APDMES-modified silica after immobilisation of MeHSi(C_5Me_4H)Cl (silica calcinated at 600°C), (b) surface **6**, APDMES-modified silica after immobilisation of MeHSi(C_5Me_4H)Cl (silica calcinated at 820°C).

In addition the IR results of surfaces **5** and **6** support the theory that $MeHSi(C_5Me_4H)Cl$ molecules can be bound both to the amine groups and directly to the surface as [silica–O–SiMeH(C_5Me_4H)] (Fig. 10). In the IR spectrum of surface **5** the Si–H band at ca. 2100 cm^{-1} is quite broad and it looks as if there are actually two bands. The main band is at 2113 cm^{-1} and can be specified as $MeHSi(C_5Me_4H)Cl$ group bound to the amine group. In the case of surface **6** the main band is at 2159 and the band at 2113 cm^{-1} is missing. The band at 2159 cm^{-1} can be assigned to the $MeHSi(C_5Me_4H)Cl$ group bound directly on the surface. In the IR spectrum of surface **5** a big new band can also be found at about 3413 cm^{-1} and is due to the N–H stretching of the secondary amine. In the case of surface **6** the band at 3413 cm^{-1} is missing, indicating that all the $MeHSi(C_5Me_4H)Cl$ groups are bound directly to the surface.

3. Conclusions

We have managed in our studies to prepare bifunctional silica surfaces, containing amine and tetramethylcyclopentadienyl functional groups. First the amine surface for silica was obtained with APDMES using saturated gas–solid reactions. At the second stage the bifunctional surface was accomplished with a reaction of silane ($Me_2Si(C_5Me_4H)Cl$ or $MeHSi(C_5Me_4H)Cl$) with the amine surface.

The modification of the amine surface with the $Me_2Si(C_5Me_4H)Cl$ and $MeHSi(C_5Me_4H)Cl$ was carried out using *n*-BuLi, which reacts with the amine groups on the modified silica surface and produces lithiated amine groups. We have noticed that *n*-BuLi also interacts with the siloxane bridges on silica surface, which results in the binding of lithium (silica–O–Li) and butyl (silica–Bu) groups on the surface. Further the tetramethylcyclopentadienylchlorosilanes react with the lithiated amine groups. On the basis of our results the $MeHSi(C_5Me_4H)Cl$ molecules also react with the surface lithium groups (silica–O–Li).

We have found that the calcination temperature has an influence on the modification of the silica surface. Naturally the calcination temperature affects the amount of Si–OH groups and thus the density of the APDMES molecules on the surface, which also has an effect on the surface reactions. For $Me_2Si(C_5Me_4H)Cl$ molecules the calcination temperature of 820°C gives the best results if we consider the total saturation of the surface amine groups. Almost every amine group has reacted with $Me_2Si(C_5Me_4H)Cl$ molecules (surface **4**). When the calcination temperature of 600°C is used the APDMES molecules are so densely populated, that due to steric hindrance $Me_2Si(C_5Me_4H)Cl$ molecules cannot react with every amine group (surface **3**).

In the case of $MeHSi(C_5Me_4H)Cl$ molecules the situation is different. $MeHSi(C_5Me_4H)Cl$ molecules appeared to react more preferably with lithium groups on the surface (silica–O–Li) than with lithiated amines probably due to the higher ionic nature of the O–Li bonds. On surface **2** (with calcination temperature of 820°C) the APDMES molecules are less densely populated so that $MeHSi(C_5Me_4H)Cl$ molecules can easily react with lithium groups on the surface (surface **6**). In the case of surface **1** (600°C) $MeHSi(C_5Me_4H)Cl$ molecules react mostly with lithiated amines because they cannot so easily reach the lithium groups on the surface (surface **5**). For this reason surface **1** (600°C) can be considered more appropriate for $MeHSi(C_5Me_4H)Cl$ molecules although the amine groups are not totally saturated with $MeHSi(C_5Me_4H)Cl$ molecules.

On the basis of our ^{29}Si-NMR results it can be concluded that $Me_2Si(C_5Me_4H)Cl$ molecules do not react with lithium groups on the surface (silica–O–Li) due to the higher steric hindrance of the two methyl groups bound to silicon.

4. Experimental

All manipulations were performed under nitrogen using vacuum line and Schlenk techniques. SiO_2 (EP 10, Crosfield Ltd.) was heat-treated in air for 16 h at 600 or at 820°C. The saturated gas–solid reactions were carried out in a commercial F-120 ALCVD reactor manufactured by Microchemistry Ltd., Finland. The solvents used were distilled from sodium benzophenone ketyl under a nitrogen atmosphere. *n*-Butyllithium was used as received. $Me_2Si(C_5Me_4H)Cl$ and $MeHSi(C_5Me_4H)Cl$ were prepared according to the literature methods [9,19,20].

IR spectra of the solid samples were recorded using a Nicolet Impact 400D FTIR spectrometer equipped with DRIFT and connected airtightly to a glovebox. The solid-state ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer equipped with a magic angle spinning probehead using the parameters described in reference [7].

4.1. Modification of silica with aminopropyldimethylethoxysilane (surface 1 and 2)

Preheated silica (8 g) in an ALCVD reactor was brought to the reaction temperature at a pressure of 6–10 kPa under a nitrogen flow. $NH_2(CH_2)_3$-$Si(CH_3)_2(OCH_2CH_3)$ (6 ml, 0.032 mol) was vaporised at 70°C and the vapour was led for 2 h through a solid silica bed supported on a sinter in a reaction chamber kept at a selected temperature [10–13] The reaction temperature was 150°C. After this, the reactor was flushed in a nitrogen stream for an additional 1 h at the reaction temperature. The sample was cooled down to room temperature (r.t.) under a nitrogen flow and transferred into a glovebox. The carbon and nitrogen content of the sample calcinated at 600°C (surface **1**) were 4.7 and 1.1% by weight, respectively the sample calcinated at 820°C (surface **2**); 3.3 and 0.7%.

^{1}H-NMR (400 MHz): δ −0.3 (Si–CH_3), 0.8 (CH_2Si and CH_2), 2.1 (CH_2N) ppm. ^{13}C-NMR (100.6 MHz): δ −2.9 (Si–CH_3), 14.3 (CH_2), 27.2 (CH_2), 45.0 (CH_2) ppm. ^{29}Si-NMR (79.5 MHz): δ 12.9 (silica–Si–CH_3), −110 (silica) ppm.

4.2. Immobilisation of (tetramethylcyclopentadienyl)-chloromethylsilanes on APDMES-functionalized silica

*4.2.1. Immobilisation of $Me_2Si(C_5Me_4H)Cl$ (surface **3** and **4**)*

Aminopropyl-functionalized silica (2 g) was degassed and purged with nitrogen. Pentane (25 ml) was added, with a double-ended needle, into the flask. Solution of *n*-BuLi [0.9 ml, 2.25 mmol (surface **3**), 0.6 ml, 1.5 mmol (surface **4**) of a 2.5 M solution in hexane] was syringed at r.t. into the stirred suspension of the aminopropyl functionalized silica. The reaction mixture was stirred overnight. The solution was filtered off and the resulting solid was washed twice with pentane. The reaction was continued directly by adding pentane (20 ml) into the flask containing the resulting solid. The solution of $Me_2Si(C_5Me_4H)Cl$ [0.48 g (surface **3**), 0.2 g (surface **4**)] in pentane (5 ml) was added into the stirred reaction mixture and stirring was continued overnight. The solution was filtered off and the resulting white solid was washed once with THF and then three times with pentane. Finally the solvent residues were evaporated under reduced pressure.

^{1}H-NMR (400 MHz): δ −0.2 (Si–CH_3), 0.8 (CH_2Si and CH_2), 1.6 (ring CH_3), 2.6 (CH_2N), 3.5 (ring CH) ppm. ^{13}C-NMR (100.6 MHz): δ −0.5 (Si–CH_3), 8.7 (ring CH_3), 13.5 (ring CH_3), 14.7 (CH_2), 26–28 (CH_2), 45.3 (CH_2), 56.2 (ring CH), 132.2 (ring C=), 134.9 (ring C=) ppm. ^{29}Si-NMR (79.5 MHz): δ 1 (Si–CH_3), 13.7 (silica–Si–CH_3), −110 (silica) ppm.

IR (cm^{-1}) 3413 (ν(N–H)), 3369 (ν(N–H)), 3300 (ν(N–H)), 2959 (ν(C–H)), 2926 (ν(C–H)), 2868 (ν(C–H)), 1634 (ν(C=C)), 1593 (δ(N–H)), 1444 (δ(C–H)), 1415 (δ(Si–CH_3)), 1378 (δ(C–H)), 1250 (δ(Si–CH_3)).

*4.2.2. Immobilisation of $MeHSi(C_5Me_4H)Cl$ (surface **5** and **6**)*

Immobilization was performed by the same procedure as in the previous case.

^{1}H-NMR (400 MHz): δ −0.5 (Si–CH_3), 0.03 (Si–CH_3), 0.8 (CH_2Si and CH_2), 1.5 (ring CH_3) 1.6 (ring CH_3), 2.4 (CH_2N), 2.7 (ring CH), 4.4 (Si–H) ppm. ^{13}C-NMR (100.6 MHz): δ −0.7 (Si–CH_3), 8.9 (ring CH_3), 12.5 (ring CH_3), 14.5 (CH_2), 26–28 (CH_2), 46.5 (CH_2), 55.2 (ring CH), 132.0 (ring C=), 135.2 (ring C=) ppm. ^{29}Si-NMR (79.5 MHz): δ −9.3 (Si–CH_3), 14 (silica–Si–CH_3), −110 (silica) ppm.

IR (cm^{-1}) 3413 (ν(N–H)), 2961 (ν(C–H)), 2924 (ν(C–H)), 2859 (ν(C–H)), 2113 (ν(Si–H)), 1635 (ν(C=C)), 1592 (δ(N–H)), 1446 (δ(C–H)), 1398 (δ(Si–CH_3)), 1386 (δ(C–H)), 881(δ(Si–H)).

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