

# Preparation of new modified catalyst carriers

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## Abstract

Novel modified catalyst carriers have been prepared. First, aminopropyltriethoxysilane (APTES) was immobilized on the silica surface by using the saturated gas–solid reactions. Secondly, two different (tetramethylcyclopentadienyl)chlorosilanes,  $(\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl})$  and  $(\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl})$ , were synthesized and anchored on the amine surface using liquid-phase reactions. Characterization of these stepwise prepared surfaces was carried out by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  solid state NMR and FTIR spectroscopy. © 1999 Elsevier Science B.V. All rights reserved.

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

## 1. Introduction

There is considerable interest in immobilization of reagents and homogeneous catalysts on organic or inorganic supports [1]. The often used method for anchoring different metal complexes on supports is the modification of surface first with a suitable ligand. A good anchoring ligand for this purpose is cyclopentadienyl group which is an important ligand in organometallic compounds. Despite of the frequency of cyclopentadienyl ligands in homogeneous organometallic compounds, these ligands have been studied only marginally as anchoring ligands on surfaces.

Our aim was to create a novel bifunctional surface that is capable to anchor different transition metal compounds. The surface was prepared stepwise, first by modifying silica with aminopropyltriethoxysilane (APTES) by utilizing the saturated gas–solid reactions [2–5], and secondly by anchoring different (cyclopentadienyl)chlorosilanes on the amine surface by using liquid-phase reactions. For the modification, we selected two quite similar (cyclopentadienyl)chlorosilanes,  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  (**1**) and  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  (**2**). These compounds were selected since they both have one chloride that can react only one way with the surface amine group. The reason why we used tetramethyl substituted cyclopentadienyls was their higher stability when compared to that of non-substituted cyclopentadienyls. Reactions of (cyclopentadienyl)chlorosilanes with different primary

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amines have been earlier investigated in association with attempts to prepare new homogeneous polymerization catalysts [6,7]. We have applied these earlier investigations in our research to synthesize novel bifunctional surfaces.

## 2. Experimental

All manipulations were performed under nitrogen using vacuum line and Schlenk techniques. SiO<sub>2</sub> (EP 10, Crosfield) was heat-treated for 16 h at 450°C in air. The saturated gas–solid reactions were carried out in a commercial F-120 ALCVD (Atomic Layer Chemical Vapor Deposition) reactor manufactured by Microchemistry, Finland. The solvents used were distilled from sodium benzophenone ketyl under nitrogen atmosphere. Me<sub>2</sub>SiCl<sub>2</sub>, MeHSiCl<sub>2</sub> and solutions of *n*-butyllithium and methyllithium were used as received. 1,2,3,4-Tetramethylcyclopentadiene (C<sub>5</sub>Me<sub>4</sub>H<sub>2</sub>), a starting material for the syntheses, was prepared according to the literature method and was degassed and purged with nitrogen before the use [8–10]. Me<sub>2</sub>Si(C<sub>5</sub>-Me<sub>4</sub>H)Cl and MeHSi(C<sub>5</sub>Me<sub>4</sub>H)Cl were prepared applying the literature methods [11,12].

IR spectra of the liquid samples were recorded as fluid films using Nicolet Magna 750 FTIR spectrometer (either diluted in dichloromethane or from neat sample). IR spectra of the solid samples were recorded using Nicolet Impact 400D FTIR spectrometer equipped with DRIFT (Diffuse Reflectance Infrared-Fourier Transform). Solution NMR spectra were measured on a Bruker AM 250 NMR spectrometer. The solid-state <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer equipped with magic angle spinning probehead using the parameters described in Ref. [13].

### 2.1. Modification of silica with APTES

Preheated silica (8.0 g) was brought to the reaction temperature at a pressure of 6–10 kPa

under a flow of nitrogen. NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub> (6 ml, 0.026 mol) was vaporized at 100°C and the vapor was led through a solid silica bed supported on a sinter in a reaction chamber kept at a selected temperature for 2 h [2–5]. 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 under a nitrogen flow and transferred into a glove-box. The carbon and nitrogen content of the sample were 5.0 and 1.5% by weight, respectively.

<sup>1</sup>H NMR (400 MHz) δ: 0.9 (CH<sub>3</sub>, CH<sub>2</sub>Si and CH<sub>2</sub>), 3.6 (OCH<sub>2</sub> and CH<sub>2</sub>N) ppm. <sup>13</sup>C NMR (100.6 MHz) δ: 9.3 (CH<sub>2</sub>), 16.0 (OCH<sub>2</sub>CH<sub>3</sub>), 26.8 (CH<sub>2</sub>), 43.3 (CH<sub>2</sub>), 58.2 (OCH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>29</sup>Si NMR (79.5 MHz) δ: –(50–64) (CH<sub>2</sub>Si), –110 (silica) ppm.

### 2.2. Preparation of (tetramethylcyclopentadienyl)chloromethylsilanes

#### 2.2.1. (Tetramethylcyclopentadienyl)dimethylchlorosilane, (I)

1,2,3,4-Tetramethylcyclopentadiene (C<sub>5</sub>Me<sub>4</sub>H<sub>2</sub>, 8 g, 0.065 mol) and pentane (110 ml) were transferred, with a double-ended needle, under a nitrogen flow, into a three-necked, 500 ml flask equipped with a dropping funnel, a magnetic stirring bar, and a gas inlet adapter. *n*-Butyllithium (26 ml of a 2.5 M solution in hexane, 0.065 mol) was added with a syringe to the solution with stirring. A white suspension of Li(C<sub>5</sub>Me<sub>4</sub>H) appeared within few minutes. The resulting suspension was stirred at room temperature for about 2 h. During the stirring the reaction mixture had turned into solid. THF (110 ml) was added and the solid mass was broken with vigorous stirring. The suspension was cooled to 0°C, and the solution of Me<sub>2</sub>SiCl<sub>2</sub> (10.2 g, 0.079 mol) in THF (22 ml) was added dropwise with stirring over an 1 h period. The resulting reaction mixture was stirred at room temperature overnight. The white solid was allowed to settle down to the bottom of the flask,

and solution was filtered with a filter cannulae technique [14]. The solvents were removed under reduced pressure. Pentane (35 ml) was added to precipitate out all of LiCl. The solution was filtered again and pentane was evaporated. Fractional distillation at 73–75°C/2 mbar yielded 9.5 g (68%) of pale yellow oil.

$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.24 (s, 6 H), 1.82 (s, 6 H), 1.98 (s, 6 H), 3.08 (s, 1 H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.63 ( $\text{CH}_3\text{Si}$ ); 11.31 (ring  $\text{CH}_3$ ), 14.34 (ring  $\text{CH}_3$ ); 56.49 (ring CH); 131.52 (C=), 137.90 (C=) ppm.  $^{29}\text{Si}$  NMR (49.7 MHz,  $\text{CDCl}_3$ )  $\delta$ : 26.83 ppm.

IR ( $\text{cm}^{-1}$ ) 2971 vs ( $\nu(\text{C-H})$ ), 2919 vs ( $\nu(\text{C-H})$ ), 2859 vs ( $\nu(\text{C-H})$ ), 1635 m ( $\nu(\text{C=C})$ ), 1547 w ( $\nu(\text{C=C})$ ), 1445 s ( $\delta_{\text{asy}}(\text{CH}_3)$ ), 1404 m ( $\delta_{\text{asy}}(\text{Si}(\text{CH}_3)_2)$ ), 1383 m ( $\delta_{\text{sy}}(\text{CH}_3)$ ), 1302 w, 1256 s ( $\delta_{\text{sy}}(\text{Si-CH}_3)$ ), 1218 m, 1124 m, 1113 m, 1053 m, 1028 m, 991 s, 957 m, 845 s ( $\gamma(\text{Si}(\text{CH}_3)_2)$ ), 815 s ( $\gamma(\text{Si}(\text{CH}_3)_2)$ ), 792 s, 739 w, 694 w, 657 s. Anal. Calcd. for  $\text{C}_{11}\text{H}_{19}\text{SiCl}$ : C, 61.51; H, 8.92. Found: C, 63.27; H, 9.46.

### 2.2.2. (Tetramethylcyclopentadienyl)chloromethylsilane, (2)

2,3,4,5-Tetramethylcyclopentadiene (13 g, 0.106 mol) and diethylether (200 ml) were transferred, with a double-ended needle, under nitrogen flow, into a three-necked, 500 ml flask equipped with a dropping funnel, a magnetic stirring bar, and a gas inlet adapter. *n*-Butyllithium (42.8 ml of a 2.5 M solution in hexane) was added dropwise to the stirred solution. The resulting mixture was stirred for 2 h meanwhile the colour of the mixture turned to ochre. More diethylether (100 ml) was added and the mixture was cooled to  $-40^\circ\text{C}$ . The solution of  $\text{HMeSiCl}_2$  (15 g, 0.13 mol) in ether (30 ml) was added gradually into the reaction mixture and stirring was continued for 2 h at  $-40^\circ\text{C}$ . At that time the mixture had turned to white in colour. The mixture was allowed to warm up to room temperature gradually and was stirred over night. The resulting precipitate was allowed to settle

down, and the solution was filtered with a filter cannulae technique. The solvent was evaporated under reduced pressure. The product was purified with fractional distillation. The colourless liquid boiling at 77–85°C (5 mbar) was collected. Yield: 10.3 g (48%).

$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$ :  $-0.06$  (d, 3 H), 1.83 (s, 6 H), 1.95 (s, 3 H), 2.01 (s, 3 H), 4.82 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ )  $\delta$ :  $-4.36$  ( $\text{CH}_3\text{Si}$ ), 11.12 (ring  $\text{CH}_3$ ), 11.32 (ring  $\text{CH}_3$ ), 13.39 (ring  $\text{CH}_3$ ), 13.78 (ring  $\text{CH}_3$ ), 54.68 (ring CH), 129.72 (C=), 132.00 (C=), 137.72 (C=), 138.49 (C=) ppm.  $^{29}\text{Si}$  NMR (49.7 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.76 ppm.

IR ( $\text{cm}^{-1}$ ) 2977 vs ( $\nu(\text{C-H})$ ), 2921 vs ( $\nu(\text{C-H})$ ), 2865 vs ( $\nu(\text{C-H})$ ), 2172 s ( $\nu(\text{Si-H})$ ), 1637 m ( $\nu(\text{C=C})$ ), 1443 s ( $\delta_{\text{asy}}(\text{CH}_3)$ ), 1400 w ( $\delta_{\text{asy}}(\text{Si-CH}_3)$ ), 1382 m ( $\delta_{\text{sy}}(\text{CH}_3)$ ), 1307 w, 1257 s ( $\delta_{\text{sy}}(\text{Si-CH}_3)$ ), 1218 m, 1126 m, 1116 m, 1054 m, 1029 m, 991 s, 953 m, 919 m, 886 s ( $\delta(\text{Si-H})$ ), 849 s, 798 m ( $\nu(\text{Si-CH}_3)$ ), 782 m ( $\gamma(\text{Si-CH}_3)$ ), 744 m, 718 m, 688 m, 668 m. Anal. Calcd. for  $\text{C}_{10}\text{H}_{17}\text{SiCl}$ : C, 59.82; H, 8.53. Found: C, 60.20; H, 9.01.

## 2.3. Immobilization of (tetramethylcyclopentadienyl)chloromethylsilanes on APTES functionalized silica

### 2.3.1. Immobilization of $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$

Aminopropyl functionalized silica (1 g) was degassed and purged with nitrogen. Pentane (10 ml) was added, with a double-ended needle, into the flask. Solution of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  (0.17 g) in pentane (4 ml) was syringed into the stirred suspension. The reaction mixture was stirred over a night. The solution was filtered off and the resulting white solid was washed three times with pentane. Finally, the solvent was evaporated under reduced pressure.

$^1\text{H}$  NMR (400 MHz)  $\delta$ :  $-0.1$  ( $\text{Si-CH}_3$ ), 0.7 ( $\text{CH}_3$ ,  $\text{CH}_2\text{Si}$  and  $\text{CH}_2$ ), 1.6 (ring  $\text{CH}_3$ ), 3.6 ( $\text{OCH}_2$  and  $\text{CH}_2\text{N}$ ) ppm.  $^{13}\text{C}$  NMR (100.6 MHz)  $\delta$ :  $-0.6$  ( $\text{CH}_3\text{Si}$ ), 9.5 (ring  $\text{CH}_3$ ), 16.3 ( $\text{OCH}_2\text{CH}_3$ ), 21–25 ( $\text{CH}_2$ ), 41.7 ( $\text{CH}_2$ ), 58.1 ( $\text{OCH}_2\text{CH}_3$ ), 131 (ring C=), 135 (ring C=)

ppm.  $^{29}\text{Si}$  NMR (79.5 MHz)  $\delta$ : 6 ( $\text{SiMe}_2$ ), –(53–64) ( $\text{CH}_2\text{Si}$ ), –110 (silica) ppm.

IR ( $\text{cm}^{-1}$ ) 2975 ( $\nu(\text{C-H})$ ), 2933 ( $\nu(\text{C-H})$ ), 2865 ( $\nu(\text{C-H})$ ).

### 2.3.2. Immobilization of $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$

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

$^1\text{H}$  NMR (400 MHz)  $\delta$ : –0.04 ( $\text{Si-CH}_3$ ), 0.8 ( $\text{CH}_3$ ,  $\text{CH}_2\text{Si-}$  and  $\text{CH}_2$ ), 1.6 (ring  $\text{CH}_3$ ), 3.6 ( $\text{OCH}_2\text{-}$  and  $\text{CH}_2\text{N}$ ), 4.4 ( $\text{Si-H}$ ) ppm.  $^{13}\text{C}$  NMR (100.6 MHz)  $\delta$ : –0.05 ( $\text{Si-CH}_3$ ), 9.7 (ring  $\text{CH}_3$ ), 16.1 ( $\text{OCH}_2\text{CH}_3$ ), 21–27 ( $\text{CH}_2$ ), 41.6 ( $\text{CH}_2$ ), 55.3 (ring  $\text{CH}$ ), 59.0 ( $\text{OCH}_2\text{CH}_3$ ), 129.9 (ring  $\text{C=}$ ), 136.1 (ring  $\text{C=}$ ) ppm.  $^{29}\text{Si}$  NMR (400 MHz)  $\delta$ : –6.0 ( $\text{SiMeH}$ ), –(53–64) ( $\text{CH}_2\text{Si}$ ), –110 (silica) ppm.

IR ( $\text{cm}^{-1}$ ) 2976 ( $\nu(\text{C-H})$ ), 2932 ( $\nu(\text{C-H})$ ), 2862 ( $\nu(\text{C-H})$ ), 2150 ( $\nu(\text{Si-H})$ ).

### 2.4. Immobilization of methylchlorosilane ( $\text{MeHSiCl}_2$ ) on APTES functionalized silica

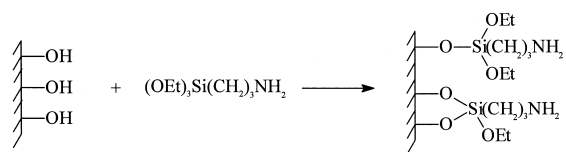
The immobilization was carried out with the same procedure as in the immobilizations of **1** and **2** on the APTES.

$^{29}\text{Si}$  NMR (79.5 MHz)  $\delta$ : –10.8, –32.2 ( $\text{SiMeH}$ ), –(55–70) ( $\text{CH}_2\text{Si}$ ), –110 (silica) ppm.

## 3. Results and discussion

### 3.1. Modification of silica with APTES

The heat treatment of silica in air at  $450^\circ\text{C}$  leads to material that contains ca. 4.1 OH groups/ $\text{nm}^2$ . About half of them are isolated OH groups and the rest hydrogen bonded OH groups [15,16]. The pretreated silica was modified with APTES in an ALCVD reactor utilizing a saturated gas–solid reaction (Scheme 1). The nitrogen analysis after modification corresponds to ca. 2.0 N atoms (or APTES molecules)/ $\text{nm}^2$  of  $\text{SiO}_2$ . In infrared spectrum (Fig. 1) the disappearance of absorption at  $3745\text{ cm}^{-1}$  is an



Scheme 1. Modification of silica surface with APTES.

evidence that most isolated  $\text{Si-OH}$  groups on the heat-treated silica are bonded to aminosilane via  $\text{Si-O-Si}$  linkages largely in a mono- and bidentate fashion as evidenced by solid state  $^{29}\text{Si}$  NMR (vide infra). In the infrared spectrum of neat APTES, the amine stretching absorptions occur at 3380, 3298 and bending at  $1606\text{ cm}^{-1}$ . The DRIFT spectrum of APTES modified silica reveals the amino stretching absorptions at 3380, 3307 and bending at  $1596\text{ cm}^{-1}$ . The broad band at  $3380\text{ cm}^{-1}$  suggests that some of the  $-\text{NH}_2$  groups are hydrogen bonded to those  $\text{Si-OH}$  surface groups which are not able to interact with the alkoxy groups of the aminosilane due to steric hindrances. The hydrocarbon IR-frequencies of the APTES modified silica are at their normal position. The absorption at  $3668\text{ cm}^{-1}$  represents the internal and hydrogen bonded  $\text{Si-OH}$  groups that cannot interact with an alkoxy silane.

In the  $^{13}\text{C}$  CP/MAS NMR spectrum of APTES, modified silica five signals can be seen: two signals of unreacted ethoxy groups at 16 and 58 ppm and three signals due to the propyl spacer ( $\text{H}_2\text{NCH}_2(1)\text{CH}_2(2)\text{CH}_2(3)\text{Si}$ ) at 44 (C1), 27 (C2) and 9 (C3) ppm [1]. In the  $^{29}\text{Si}$  spectrum the silicon resonance of silica can be seen at –110 ppm and the signals of APTES at –52 and –58 ppm corresponding to the mono- and bidentate forms, respectively.

### 3.2. Synthesis of functionalizing agents

The reactions of lithiated tetramethylcyclopentadiene ( $(\text{C}_5\text{Me}_4\text{H})^-\text{Li}^+$ ) with dimethyldichlorosilane ( $\text{Me}_2\text{SiCl}_2$ ) and methyldichlorosilane ( $\text{MeHSiCl}_2$ ) lead to the monosubstituted cyclopentadienylsilanes (Scheme 2),  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  (**1**) and  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$

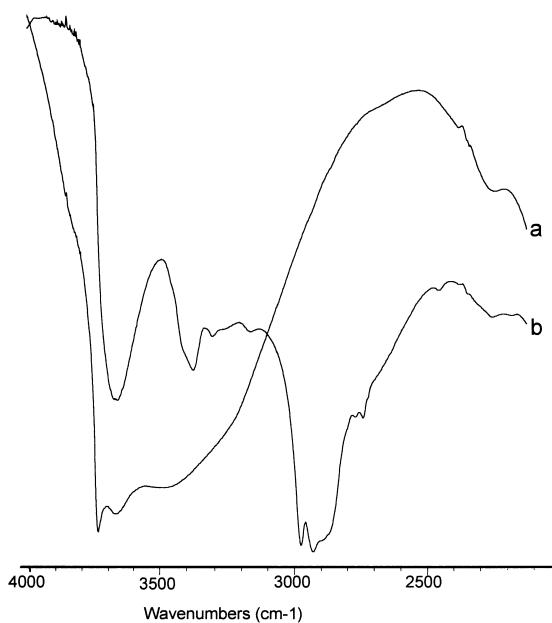


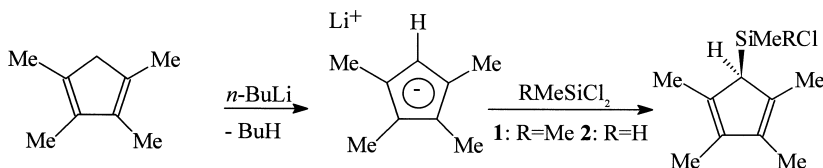
Fig. 1. IR spectra of (a) heat treated (450°C) neat silica, (b) APTES modified silica.

(2), respectively. The synthesis of **1** was based on the known method [11,12] which was slightly modified. The new compound **2** was synthesized with a similar method. Reaction conditions, especially solvent and temperature, play a big role in the syntheses. For example, methylchlorosilane ( $\text{MeHSiCl}_2$ ) is more reactive than dimethylchlorosilane and therefore the reaction temperature had to be lower. Characterization of the compounds was based on  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR. Earlier investigations [17] have proved that if there is oligomethylene spacer between the Cp ring and the silicon atom ( $\text{Si}(\text{CH}_2)_n\text{-Cp}$ ), the synthesis gives various structural isomers. According to  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR spectra in the cases of **1** and **2** the syntheses

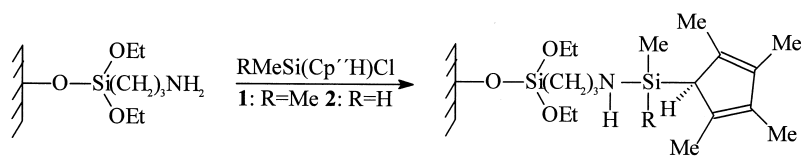
produce only one product. There is only one resonance in the  $^{29}\text{Si}$  NMR spectra of both **1** and **2**. In the  $^{13}\text{C}$  NMR spectrum of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$ , two methyl signals of the ring at  $\delta$  11 and 14 ppm can be seen as well as two signals of the quaternary carbon atoms of the double-bonds of the ring at  $\delta$  131 and 138 ppm. The  $^{13}\text{C}$  NMR spectrum of  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  differs from former case considerably. There can be found four signals due to the methyl groups of the ring (between  $\delta$  11 and 14 ppm) and four due to the quaternary carbon atoms of the double-bonds of the ring (between  $\delta$  129 and 139 ppm). The spectra can be explained with the higher symmetry of the structure in  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  and with the asymmetry of the structure in the case of  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$ . IR spectrum is especially important for the identifying  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$ . The band at  $2170\text{ cm}^{-1}$  belongs to the proton attached to the silicon atom. There are no other bands in this area of the spectrum, so the band can easily identified even when the molecule is bound on to the silica surface.

### 3.3. Immobilization of (tetramethylcyclopentadienyl)methylchlorosilanes on APTES functionalized silica

The reaction of (cyclopentadienyl)chlorosilanes with amine group of the modified silica surface produces a chemical bond between nitrogen and silicon and as a by-product HCl is formed (Scheme 3). Characterization of the new surfaces has been done with solid-state CP/MAS NMR and IR spectroscopy.



Scheme 2. Preparation of (tetramethylcyclopentadienyl)chloromethylsilanes.



Scheme 3. Immobilization of (tetramethylcyclopentadienyl)methylchlorosilanes on APTES functionalized silica.

The key information for analysing the surfaces comes from  $^{13}\text{C}$  NMR spectroscopy. The  $^{13}\text{C}$  NMR spectrum of immobilized  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  on the APTES functionalized silica (Fig. 2) shows two resonances of the quaternary carbon atoms of the double bonds of the ring ( $\delta$  131 and 135 ppm). The signal of the silicon bound methyl groups ( $\text{CH}_3$ ) appears at about  $-0.6$  ppm. At the chemical shift range between  $\delta$  9 and 25 ppm can be found several resonances which are difficult to be assigned individually. We assume that the signal at  $\delta$  21 ppm belongs to the methylene ( $\text{CH}_2$ ) group of the APTES. The signal at about  $\delta$  9 ppm is assigned for methyl groups of the ring. The

signal at  $\delta$  16 ppm belongs to the methyl group of the ethoxy group. The signal of the C3 methylene group is overlapped by the methyl signals of the ring ( $\delta$  8–13 ppm). A signal due to aliphatic methane carbon of the ring ( $\text{CH}$ ) was not found because it is probably obscured by the methylene signal of the ethoxy group.

In the  $^{29}\text{Si}$  CP/MAS NMR spectrum of the immobilized  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  (Fig. 3), a broad resonance at  $\delta$   $-(50\text{--}70)$  ppm can be found corresponding to the APTES bound to silica. The resonance refers to mono-, bi- and tridentate bindings of APTES. The chemical shift of the  $-\text{SiMe}_2(\text{C}_5\text{Me}_4\text{H})$  moiety can be found at about  $\delta$  6 ppm. Furthermore, a broad signal at about  $\delta$   $-15$  ppm can be found in the spectrum. This signal has been identified to belong to  $-\text{SiMe}_2\text{Cl}$  and  $=\text{SiMe}_2$  groups bound to amine in a mono- and bidentate style based on our own observations. We have noticed that the presence of the hydrogen chloride in the

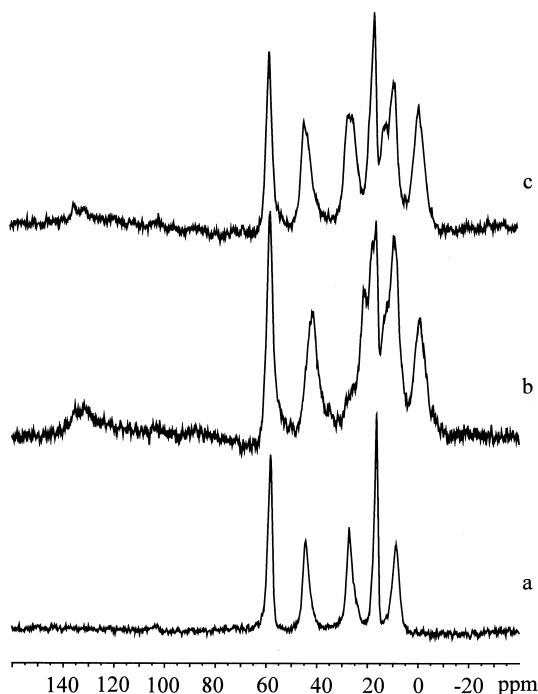


Fig. 2. CP/MAS NMR  $^{13}\text{C}$  NMR spectra of (a) APTES modified silica, (b) APTES modified silica after immobilization of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$ , (c) b after MeLi treatment.

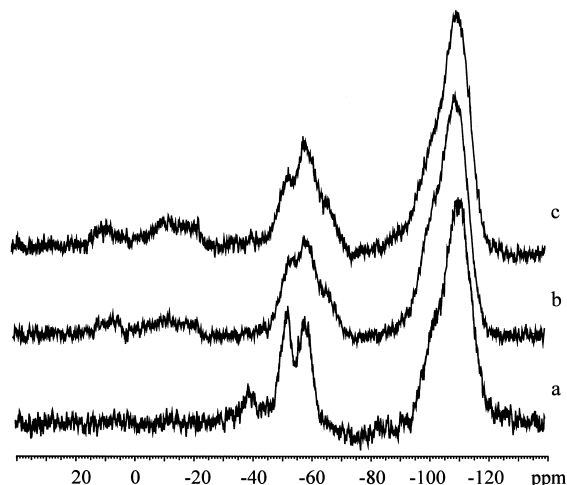


Fig. 3. CP/MAS NMR  $^{29}\text{Si}$  NMR spectra of (a) APTES modified silica, (b) APTES modified silica after immobilization of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$ , (c) b after MeLi treatment.

immobilization of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  molecule can cause a cleavage of the Cp–Si bond.

Immobilization of  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  on the APTES functionalized silica takes place similarly to that of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  based on  $^{13}\text{C}$  NMR spectrum (Fig. 4). The  $^{13}\text{C}$  signal of the methyl group bound to silicon of the  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})$ -group appears at  $\delta -0.1$  ppm. In this case, the band of the aliphatic methane carbon (CH) of the  $(\text{C}_5\text{Me}_4\text{H})$ -ring can also be found at about  $\delta 55$  ppm. The  $^{29}\text{Si}$  CP/MAS NMR spectrum (Fig. 5) shows the resonances of the APTES bound to silica at the chemical shift range  $\delta -(50-70)$  indicating the mono-, bi- and tridentate binding of APTES. According to  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra the number of ethoxy groups has diminished during the immobilization indicating more the bi- and tridentate binding. The resonance at  $\delta -6$  ppm has been assigned to the  $-\text{SiMeH}(\text{C}_5\text{Me}_4\text{H})$  moiety. According to our observation, in the case of  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$ , the Cp–Si bond cleavage

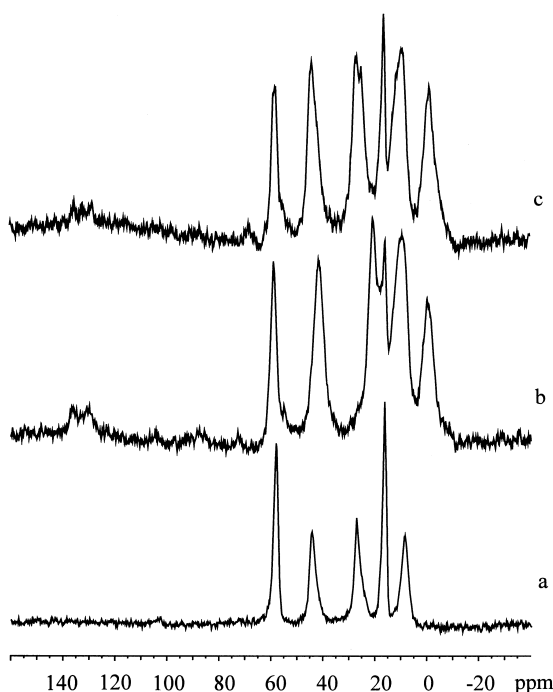


Fig. 4. CP/MAS NMR  $^{13}\text{C}$  NMR spectra of (a) APTES modified silica, (b) APTES modified silica after immobilization of  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$ , (c) b after MeLi treatment.

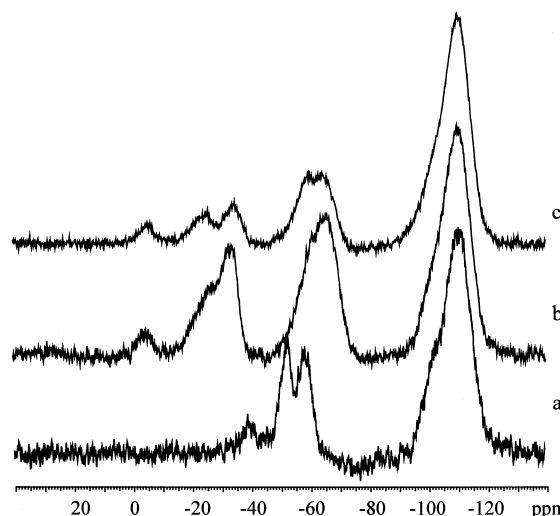


Fig. 5. CP/MAS NMR  $^{29}\text{Si}$  NMR spectra of (a) APTES modified silica, (b) APTES modified silica after immobilization of  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$ , (c) b after MeLi treatment.

happens even to a larger extent than in the case of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  molecule. In the  $^{29}\text{Si}$  CP/MAS NMR spectrum, a big signal at about  $\delta -30$  ppm can be seen. The  $^{29}\text{Si}$  NMR spectrum of immobilized  $\text{MeHSiCl}_2$  on the APTES modified silica contains the same resonance at  $\delta -30$  ppm as in the case of **2** on the APTES. This proves the cleavage of the Cp–Si bond and the wide resonance can be assigned to  $-\text{SiMeHCl}$  and  $=\text{SiMeH}$  groups bound to amine in a mono- or bidentate forms. From the IR spectrum of  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  on the APTES, modified silica can be found the band which belong to the proton attached to the silicon atom at  $2150\text{ cm}^{-1}$  (Fig. 6).

The shape of the IR spectra in the area of  $3000\text{ cm}^{-1}$  gives some information about the binding of (tetramethylcyclopentadienyl)chlorosilanes on the surface (Figs. 6b and 7b). Immobilization of  $\text{Me}_2\text{HSiCl}$  on an APTES modified oxidized aluminium substrate has been found to produce dimethylsilane-ammonium salt forms (Scheme 4) [18,19]. Utilizing this information, we have deduced that protonated salt form can also be formed in our case. Hydrogen chloride which releases in the reaction binds to the amine group and this protonated form causes the broad

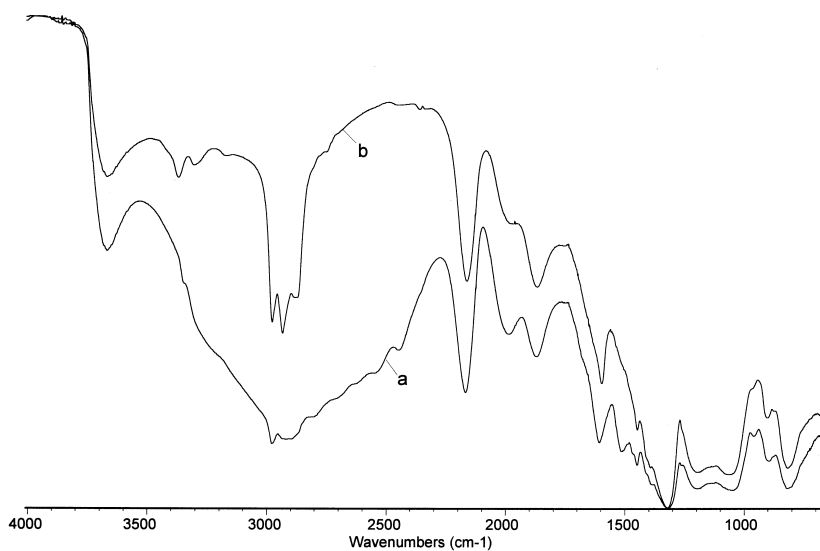


Fig. 6. IR spectra of (a) APTES modified silica after immobilization of MeHSi(C<sub>5</sub>Me<sub>4</sub>H)Cl, (b) a after MeLi treatment.

shape of the IR spectra around 3000 cm<sup>-1</sup>. The <sup>13</sup>C NMR spectra in Figs. 2 and 4 also indicate the presence of the protonated form. According to literature, the presence of HCl on the APTES modified silica induces changes in the <sup>13</sup>C NMR spectrum, especially the C2 resonance of the aminopropyl chain becomes sharper and is shifted to higher field [20,21]. We have also observed this same phenomenon in the <sup>13</sup>C NMR

spectra (Figs. 2 and 4). The protonated form can be released by treating the modified silica with methyllithium (MeLi). This treatment shifts the C2 resonance of the aminopropyl chain back to downfield from about 21 to 26 ppm. Influence of the MeLi treatment could be noticed also from IR and <sup>29</sup>Si NMR spectra. The shape of the IR spectra changed considerably in the area of 3000 cm<sup>-1</sup> as can be seen from the Figs. 6

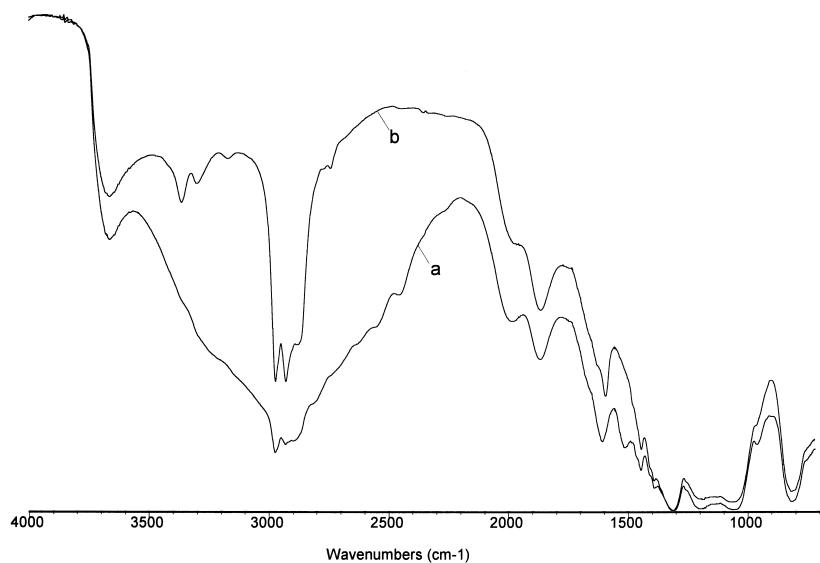
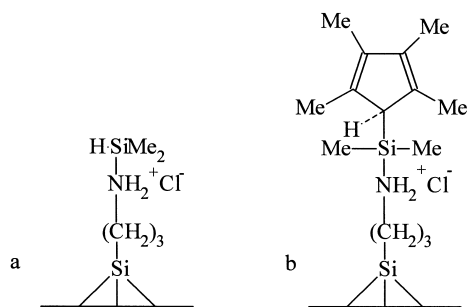


Fig. 7. IR spectra of (a) APTES modified silica after immobilization of Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>H)Cl, (b) a after MeLi treatment.





Scheme 4. (a) Dimethylsilane-ammonium salt form at oxidized aluminium substrate [15,16]. (b) Protonated salt form after immobilization of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  on APTES modified silica.

and 7.  $^{29}\text{Si}$  NMR spectrum, specially in the case of immobilized  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  (Fig. 5), changed after  $\text{MeLi}$  treatment in the area of  $\delta$   $-(20-40)$  ppm, where the resonances due to the  $-\text{SiMeHCl}$  and  $=\text{SiMeH}$  type of structures decreased.

#### 4. Conclusions

Our aim was to create a novel bifunctional surface that is capable to anchor different transition metal compounds. We managed to modify silica surface with APTES with a new method (ALCVD) and further to immobilize two different silanes,  $(\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl})$  (**1**) and  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  (**2**), on the amine surface. In any way, we faced some obstacles in the immobilization process. The reaction of amine group on the modified silica surface with (cyclopentadienyl)chlorosilanes produced a chemical bond between nitrogen and silicon and as a by-product HCl was formed. This HCl caused problems because it attached to the amine group and caused formation of a protonated salt, which fortunately can be released with  $\text{MeLi}$  treatment. Another disadvantage caused by HCl was the cleavage of the  $\text{Cp}-\text{Si}$  bond. This problem can be solved by carrying out the reaction in such way that HCl will not form. We have tried to immobilize the silanes,  $(\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl})$  (**1**) and  $\text{MeHSi}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  (**2**), on

the APTES modified silica by using *n*-butyllithium (BuLi). In this method, HCl does not form but we faced some other problems with the unreacted ethoxy groups. We noticed that also the unreacted ethoxy groups reacted with the BuLi. In the future, we are going to use amines which do not contain unreacted ethoxy groups, such as aminopropyltrimethoxysilane (APDMES), and in that way we can avoid the problems faced in this work.

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