Silica hydride intermediate for octadecylsilica and phenyl bonded phase preparation via heterogeneous hydrosilation in supercritical carbon dioxide

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ABSTRACT

Investigations into the preparation of silica hydride intermediate in supercritical carbon dioxide (sc-CO_2) that avoids the use of organic solvents such as toluene or dioxane are described. The effects of reaction temperature, pressure and time on the surface coverage of the supercritical fluid generated silica hydride intermediate were studied. Under optimised supercritical conditions of 120 °C, 483 bar and 3 h reaction time, silica hydride (Si–H) conversion efficiencies of *ca.* 40% were achieved for the hydride intermediate prepared from a monofunctional silane reagent (dimethylmethoxysilane). Si–H conversion efficiencies (as determined from ^{29}Si CP-MAS NMR spectral analysis) for the hydride intermediate prepared from triethoxysilane (TES) in sc-CO_2 were found to be comparable to those obtained using a TES silanisation approach in an organic solvent. ^{13}C and ^{29}Si CP-MAS-NMR spectroscopy was employed to provide a complete structural assignment of the silica hydride intermediates. Furthermore, supercritical CO_2 was subsequently employed as a reaction medium for the heterogenous hydrosilation of silica hydride with octadecene and with styrene, in the presence of a free radical initiator. These supercritical fluid generated reversed-phase materials were prepared in a substantially reduced reaction time (3 h) compared to organic solvent based methods (100 h reaction time). Silica functionalisation in sc-CO_2 presents an efficient and clean alternative to organic solvent based methods for the preparation of important silica hydride intermediate and silica bonded stationary phases via a hydrosilation approach.

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1. Introduction

Supercritical carbon dioxide (sc-CO_2) is an effective and clean reaction medium for the preparation of chromatographic stationary phases. It has previously been demonstrated that this "green" solvent approach can be successfully exploited for the preparation of alkyl and fluorinated alkyl phases [1,2], a chiral stationary phase via a mercaptopropyl bonded silica intermediate [3], and for polar embedded and dendritic phases [4,5].

There has been a steady growth in interest in the use of supercritical carbon dioxide as a cleaner reaction medium for bonded phase synthesis for over a decade now. Yarita et al. demonstrated a method for endcapping octadecylsilyl (ODS)-silica gels using supercritical carbon dioxide as a silylation medium [6], while Robson et al. prepared bonded silica stationary phases in sc-CO_2 using an autoclave at 150 degrees for 20 h [7]. Healy et al. exploited the high diffusivity and mass transfer kinetics of sc-CO_2 to generate fluorinated octyl, and endcapped and non-endcapped C_{18} (C 20.58%) silica bonded phases using this supercritical fluid technology (60 °C, 450 bar, 3 h). These sc-C_{18} bonded phases were subsequently employed for the highly efficient separation of a standard reversed-phase test mixture (141,000 N/m for fluorene) and the rapid separation of four analgesics in less than 3 min [1].

It has been demonstrated that sc-CO_2 is comparable or better than organic solvents for silanisation reactions with silica [8]. McCool and Tripp have reported that inaccessible silanols are accessible in sc-CO_2 [9]. Tripp and co-workers have studied the reaction of organosilanes with silica in sc-CO_2 using infrared techniques [10,11]. Gu and Tripp highlighted the effectiveness of silanisation with silica in sc-CO_2 by investigating the reaction of organosilanes with other metal oxides such as alumina and titania [12].

The catalytic coupling of unsaturated organic compounds onto a silica hydride intermediate to form hydrolytically stable Si–C linkages, pioneered by Joseph Pesek, is now a key synthetic route to silica bonded stationary phases for liquid chromatography and also to functionalised capillaries for capillary electrophoresis [13,14]. This two step process firstly involves the introduction of hydride groups onto the silica surface. The covalent attachment of the

desired organic compound, in general via a terminal olefin, onto the hydride silica surface is typically facilitated by the use of Speier's catalyst (a 2-propanol solution of hexachloroplatinic acid) [15]. A free radical initiator or a peroxide catalyst offers an alternative to this transition metal catalyst for the generation of a silica bonded phase [15].

This silanation/hydrosilation approach has been utilised to produce a wide variety of silica bonded phases [16–19]. Hydrosilation of alkynes has been exploited as a means of introducing a bidentate linkage onto a phase [20]. It has been reported that the successful conversion of surface silanols to surface silica hydride groups is the key to producing an effective bonded phase for chromatography [21]. Silica functionalisation must result in a high coverage of hydride groups on the surface as the amount of these hydride groups will determine the phase loading of the final bonded phase.

Hydride functionality can be introduced onto the silica surface via the chlorination of silica with thionyl chloride followed by reduction using $LiAlH_4$ [22,23]. However, this two-step method is moisture sensitive and produces volatile reduction byproducts such as sulphur dioxide [24]. Chu and Pesek demonstrated the reaction of a trisubstituted silane such as triethoxysilane (TES) with silica in the presence of water, and an acid catalyst such as HCl in dioxane [24]. The reaction mechanism involves the generation of a silanetriol species ($HSi(OH)_3$) by the hydrolysis of the trisubstituted silane. The silanetriol is then covalently attached to the silica surface and the adjacent silanols via a series of condensation reactions. The unique properties of silica hydride and its bonded phases in a variety of chromatographic applications and formats have been recently reviewed [19]. New approaches to the preparation of silica hydride continue to be of interest [25], including an effective high-temperature chlorination-reduction sequence for the preparation of silicon hydride modified silica surfaces which has also recently been reported [26].

Supercritical carbon dioxide (sc-CO_2) is an advantageous substitute to organic solvents as it is non-flammable, more environmentally friendly, inexpensive, less hazardous and can be easily recycled [27,28]. The density and therefore the solubility of many compounds in sc-CO_2 can be readily controlled by varying reaction temperature and pressure.

This research presents the first examples of the preparation of a silica hydride intermediate and subsequent heterogenous hydrosilation reactions under supercritical fluid conditions, eliminating the use of organic solvents in the process of reaction and product isolation/cleanup. Both mono and trifunctionally prepared silica hydride intermediates were prepared and characterised using solid state NMR, DRIFT spectroscopy and thermal analysis. Furthermore, the chromatographic performance of an octadecylsilica column, prepared entirely using sc-CO_2, via free radical mediated hydrosilation, endcapping and column packing is demonstrated.

2. Experimental

2.1. Materials

Porous silica particles, Exsil-Avanti silica (3 μm, 205 m^2/g, 130 Å) was purchased from Alltech/Exmere (Lancashire, UK). Dimethylmethoxysilane (DMMS) and triethoxysilane (TES), which were used to prepare the silica hydride intermediates were obtained from Fluorochem (Derbyshire, UK). HPLC grade acetonitrile was obtained from Sigma–Aldrich (Dublin, Ireland). All water was distilled and deionised to a resistivity of 18.2 $M\Omega$ cm. Uracil, phenol, pyridine, benzamide, benzophenone, biphenyl, hexamethyldisilazane, octadecene, styrene, theophylline, 4-nitroaniline, methyl benzoate, phenetole and o-xylene were purchased from Sigma–Aldrich (Dublin, Ireland). CO_2 was obtained from Irish Oxygen (Cork, Ireland). Mobile phases were ultrasonically degassed and filtered prior to use using Millipore 0.45 μm filters, which were obtained from Millipore (Cork, Ireland).

2.2. Instrumentation

Reactions in sc-CO_2 were carried out using an Isco model 260D syringe pump with an external 25 ml stainless steel reaction cell with 0.625" sapphire windows at either end of the reaction cell, all of which were obtained from Thartech Inc. (USA). The temperature of the reaction cell was controlled using a Horst heating tape (1 m in length) connected to a Horst temperature controller, which made contact with the reaction cell via a thermocouple. These were obtained from Sigma–Aldrich (Dublin, Ireland). Agitation was achieved by gentle stirring with a Teflon coated magnetic stirrer bar in the reaction cell and a magnetic stirrer plate underneath the cell. The magnetic stirrer plate without heating (Midi-MR 1 digital IKA-MAG) was purchased from Ika Werke Gmbh & Co. KG (Germany). All chromatography was performed on an Agilent 1100 series LC, with quaternary pump and diode array UV detector.

2.3. Preparation of silica hydride intermediates and bonded phases

2.3.1. Preparation of silica hydride intermediates in sc-CO_2

Exsil-Avanti silica (1.0 g), a magnetic stirrer bar and chosen silane were added to a 25 ml stainless steel reaction cell. The quantity of silane reagent used was generally a five mole equivalent. Thus for 1.0 g amount of silica, 0.8 g of the monofunctional silane, dimethylmethoxysilane (DMMS) was utilised or 1.4 g of triethoxysilane (TES).

The temperature of the reaction cell was raised beyond the critical temperature of CO_2 (31.2 °C) when above the critical pressure of CO_2 (73.8 bar). Supercritical reactions were carried out at 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C and 120 °C while other reactions conditions remained constant at 414 bar and a reaction time of 3 h. In addition, reactions were conducted at different reaction pressures from 138 bar, 207 bar, 276 bar, 345 bar, 414 bar and 483 bar while other reaction conditions remained constant at 100 °C and a reaction time of 3 h. Supercritical reactions were also conducted at 1 h, 3 h and 5 h while other reaction conditions remained constant at 100 °C and 483 bar. The magnetic stirrer plate ensured gentle agitation of the contents of the cell (600 rpm), which was visually verified by looking through the sapphire windows at either end of the reaction cell. Following the chosen reaction time, the magnetic stirrer was switched off to allow the contents of the cell to settle for several minutes, after which the cell mixture was subjected to dynamic extraction. During this extraction period, the pressure and temperature of the reaction cell were maintained and *ca.* 120 ml of fresh CO_2 was flushed through the cell at a flow rate of approximately 5 ml/min. Thus, the total duration of dynamic extraction was between 20 and 25 min. After this time, the cell was then depressurised and the bonded silica offloaded as a free flowing white powder, for characterization and further reaction.

2.3.2. Preparation of silica hydride intermediate in dioxane

Exsil Avanti silica (1.0 g) was placed in a 3-neck 100 ml round bottom flask with 20 ml of dioxane and a magnetic stir bar. 1.5 ml of aqueous 2.3 M hydrochloric acid solution was added. The mixture was heated to 70–80 °C under reflux. 9 ml of 0.5 M silane/dioxane solution was added dropwise over a period of 15–20 min using an addition funnel. The mixture was refluxed for 3 h at 100 °C. After this time the product was filtered and washed consecutively with 50 ml portions of 20:80 water/tetrahydrofuran, tetrahydrofuran and methanol (twice with each solvent). The resulting white powder was dried overnight under vacuum.

2.3.3. Preparation of endcapped C_{18} and phenyl stationary phases by hydrosilation in sc-CO_2

The monofunctionally prepared silica hydride was chosen for hydrosilation with octadecene under supercritical conditions based on amounts utilised by the procedure developed in organic solvents, employing AIBN as a free radical initiator [15]. The reaction cell containing the olefin and the free radical initiator was sealed and the heating tape was wrapped around the body of the reaction cell. The magnetic stirrer plate was switched on, thus ensuring the agitation of the contents of the cell (600 rpm), which was visually verified by looking through the sapphire windows at either end of the reaction cell. The temperature of the reaction cell containing the olefin and the free radical initiator was raised to 70 °C and maintained at this temperature with agitation for a period of 40 min. After this time, the magnetic stirrer was switched off so as to allow the contents of the cell to settle for several minutes, after which the reaction cell was opened. The supercritical fluid generated silica hydride intermediate was then added to the contents of the reaction cell through the open neck of the stainless steel reaction cell. The cell was closed tightly and the temperature of the cell mixture was raised beyond the critical temperature (31.2 °C) and pressure (73.8 bar) of CO_2. The contents of the reaction cell were maintained under supercritical conditions of 70 °C and 414 bar with agitation for a period of 3 h. After this period of time, the magnetic stirrer was switched off so as to allow the contents of the cell to settle for several minutes, after which the cell mixture was subjected to a dynamic extraction. During this extraction period, the pressure and temperature of the reaction cell were maintained and *ca.* 60 ml of fresh CO_2 was flushed through the cell at a flow rate of approximately 5 ml/min. After this time, the cell was then depressurised and the bonded silica offloaded as a free flowing white powder.

To further illustrate the utility of sc-CO_2, a phenyl phase was prepared by the hydrosilation of styrene with the TES silica hydride intermediate using AIBN, under the following supercritical fluid conditions. The reaction mixture of silica hydride (1.0 g), styrene (1.12 g) and AIBN (0.08 g) was subjected to supercritical reaction conditions of 70 °C, 414 bar for 3 h with agitation (600 rpm). Following the chosen reaction time, the contents of the cell were allowed to settle for several minutes and then subjected to a dynamic extraction with *ca.* 120 ml of fresh CO_2 was flushed through the cell at a flow rate of approximately 8 ml/min. Following dynamic extraction, the cell was then depressurised and the bonded silica offloaded as a free flowing white powder.

The C_{18} functionalised silica was endcapped under supercritical conditions of 70 °C, 414 bar for 2 h using hexamethyldisilazane (based on 1.5 mol equiv. of surface silanols). Following the chosen reaction time, the contents of the cell were allowed to settle for several minutes and then subjected to a dynamic extraction with *ca.* 120 ml of fresh CO_2 was flushed through the cell at a flow rate of approximately 5 ml/min. Following dynamic extraction, the cell was then depressurised and the bonded silica offloaded as a free flowing white powder.

Elemental analysis of the endcapped sc-C_{18} silica gave: C, 18.0%; H, 3.0%.

Elemental analysis of the sc-phenyl silica gave: C, 17.4%; H, 1.9%.

2.4. Characterisation of bonded silicas prepared in sc-CO_2

2.4.1. Percent carbon

Elemental analysis of bonded silica samples was performed on a Perkin-Elmer 240 elemental analyser at the Microanalytical Laboratory, Chemistry Department, UCC (Cork, Ireland).

2.4.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) experiments were performed on a Polymer Laboratories Ltd., Model TGA1000M analyser

at the Tyndall National Institute (Cork, Ireland). A sample of bonded silica (5–10 mg) was placed on a pre-tared Inconel sample pan and the weight recorded. The sample was heated from 25 °C to 800 °C using a linear gradient at a heating rate of 40 °C/min. TGA samples were separately analysed under inert (N_2) and oxidising (air) conditions at a flow rate of 25 ml/min and 60 ml/min, respectively.

2.4.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were carried out on a Pyris 1 Model DSC instrument at the Tyndall National Institute (Cork, Ireland). A sample of bonded silica (1–5 mg) was loaded onto a pre-tared aluminium crucible and the weight recorded. The bonded silica sample in the aluminium crucible was encapsulated with an aluminium lid and crimped (sealed). The sample was heated from 25 °C to 600 °C at a heating rate of 30 °C/min. DSC experiments were performed under oxidising (air) and inert (N_2) conditions at flow rates of 70 ml/min and 25 ml/min, respectively.

2.4.4. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy

DRIFT spectra were obtained on a BioRad model FTS 3000 FT-IR spectrometer (Biorad Laboratories, Cambridge, USA) with a DRIFT attachment (Pike Technologies, USA). KBr was ground to a fine powder using a pestle and mortar. A DRIFT sample holder (width: 6 mm; depth: 2 mm) was filled with KBr, the surface of which was levelled and subsequently utilised to record the background spectra. The bonded silica material was mixed with KBr at a ratio of 1:30, ground to a fine powder and a DRIFT sample holder was filled and the surface levelled. All spectra were run from 4000 cm^{-1} to 400 cm^{-1} at a scan rate of 16 s^{-1} and a resolution of 4 cm^{-1}.

2.4.5. Nuclear magnetic resonance spectroscopy

^{13}C and ^{29}Si CP-MAS NMR spectra were carried out by Mr. Benjamin Dietrich of Professor Dr. Klaus Albert's research group of the Institut für Organische Chemie, Universitat Tübingen, Tübingen, Germany. Solid state ^{29}Si NMR measurements were performed on a ASX 300 spectrometer (Bruker, Rheinstetten, Germany), and ^{13}C on a DSX 200 spectrometer (Bruker, Rheinstetten, Germany), using cross polarisation and magic angle spinning (CP-MAS). For the ^{29}Si nucleas, a contact time of 5 ms and a pulse repetition time of 1.5 s were employed and for ^{13}C, a contact time of 3 ms and repetition time of 2 s. Frequencies of 75.5 and 59.6 MHz for carbon and silicon, respectively, were used. Representative samples of 200–250 mg were spun at 4 kHz using 7 mm double bearing ZrO$_2$ rotors. Typically, 1.5 k free induction decays (FIDs) with an acquisition time of 35 ms were accumulated in 1 kilobyte (kb) data points and zerofilling to 8 kb prior to Fourier transformation. The line broadening used was 30 Hz and the spectral width for all spectra was about 25 kHz. All chemical shifts were referenced to Q_8M_8.

2.5. Column packing conditions

The sc-CO_2 generated silica hydride intermediate which was prepared using a trifunctional silane (TES) was packed into a stainless steel LC column of dimensions 2.1 mm I.D. × 50 mm by Waters Technologies Ireland Ltd. (Wexford, Ireland).

The endcapped sc-C_{18} silica was packed into a stainless steel LC column of dimensions 2.1 mm I.D. × 50 mm, using the supercritical fluid slurry packing technique. The LC column to be packed was connected (via stainless steel tubing) to another stainless steel LC column which served as the packing reservoir due to its larger dimensions (4.6 mm I.D. × 10 mm). This reservoir contained the endcapped sc-C_{18} bonded silica packing material. The reservoir was connected to the sc-CO_2 syringe pump thus facilitating the introduction of pressurised CO_2. The end of the LC column to be
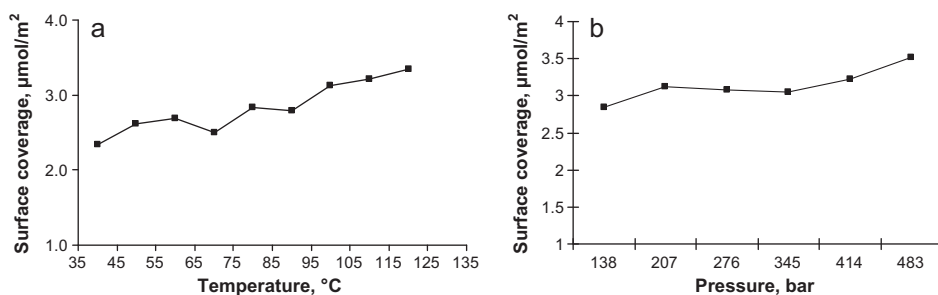
Fig. 1. (a) Effect of reaction temperature (414 bar, 3 h) and (b) the effect of reaction pressure (100 °C, 3 h) on surface coverage values for monofunctionally prepared silica hydride intermediate prepared in sc-CO$_2$ (Exsil-Avanti silica and DMMS).

packed was connected to a short length of stainless steel tubing which served as a restrictor. The LC column and restrictor were immersed in an ultrasonic bath, set at a temperature above the critical value for CO$_2$ (*T$_c$*: 31.1 °C), approximately 60 °C. The sc-CO$_2$ was introduced at an initial pressure of 104 bar, which was maintained for 1 min. The pressure was increased stepwise to 173 bar, 242 bar, 311 bar and finally to a pressure of 345 bar. Thus the pressure inside the LC column was maintained at a pressure above the critical value for CO$_2$ (*P$_C$*: 72.8 bar). Under low supercritical pressures, the sc-CO$_2$ was observed exiting from the restrictor tubing. As the pressure increased, the flow of sc-CO$_2$ decreased from the restrictor as the column packing progressed. The pressure of 345 bar was maintained for a period of 45 min. Following column packing, the pressure was discontinued and the LC column was allowed to slowly depressurise over a period of 1 h.

The sc-phenyl silica was packed into a stainless steel column of dimensions 4.6 mm I.D. × 50 mm using 100 ml isopropyl alcohol at 414 bar. The column was then inverted and the packing continued with 100 ml of a mixture methanol–water (50:50), which was also used as the conditioning solvent at a ratio of (60:40).

2.6. Chromatographic evaluation

Standard reversed-phase mixtures of benzamide, benzophenone and biphenyl were eluted on the sc-endcapped C$_{18}$ stationary phase using a mobile phase mixture of methanol/water, at a flow rate of 0.5 ml/min at 25 °C with UV detection at 254 nm.

A mixture of theophylline, 4-nitroaniline, methyl benzoate, phenetole and o-xylene was separated on the sc-phenyl stationary phase using a mobile phase mixture of acetonitrile/water (30:70), at a flow rate of 1.0 ml/min at 25 °C with UV detection at 254 nm.

3. Results and discussion

3.1. Optimisation of sc-CO$_2$ reaction conditions for a monofunctionally prepared silica hydride intermediate

Supercritical fluids are "tunable" solvents, in that their bulk properties such as solvent density and solvating power can be varied by small changes in reaction temperature and pressure. Supercritical reaction parameters such as reaction temperature, pressure and the duration of the reaction were initially investigated for the reaction of Exsil-Avanti 3.0 μm porous silica particles and a monofunctional silane (DMMS). The surface coverage for silica hydride intermediates prepared using a monofunctional silane were calculated using an equation derived by Berendsen and de Galan [24,29,30]. Surface coverage for the monofunctionally prepared silica hydride (Fig. 1) increased as a function of increasing temperature from 40 °C to 120 °C (constant pressure and duration of 414 bar, 3 h) and of increasing pressure from 138 bar to 483 bar (constant temperature and duration of 100 °C, 3 h). The highest

surface coverage value for this monofunctionally prepared silica hydride intermediate of 3.5 μmol/m^2 (C 1.6%), was obtained under supercritical reaction conditions of high temperature and pressure (120 °C, 483 bar, 3 h). Under these supercritical conditions of high temperature and pressure, the solvent density and thus the solvating power of sc-CO$_2$ is at a maximum for the supercritical reaction conditions which were examined for this silanisation reaction. Due to the high diffusivity of sc-CO$_2$, the monofunctional silylating reagent (dimethylmethoxysilane) can access silica surface silanols and undergo silanisation much more readily under these conditions as the silane is highly solubilised in the supercritical fluid.

The surface coverage value of 3.5 μmol/m^2 represents a conversion efficiency of *ca.* 43% of surface silanols (Si–OH) to silica hydride (Si–H) based on silanol content of native silica of 8.0 ± 1.0 μmol/m^2. Typical monomeric silica bonded phases yield a silanol conversion efficiency of no greater than 40–50% [31]. From the series of studies carried out here using DMMS and from our previous work with DMES [32], the silanol conversion efficiency achieved for sc-CO$_2$ generated silica hydride intermediate is comparable, and indeed superior (for certain silica materials) to those obtained using organic solvent based methods (Table 1).

3.2. Solid state ^{29}Si and ^{13}C CP-MAS NMR, DRIFT and thermal analysis of sc-CO$_2$ silica hydride

3.2.1. ^{29}Si and ^{13}C CP-MAS NMR investigations of a monofunctionally prepared silica hydride intermediate

The ^{29}Si CP-MAS NMR spectrum for the silica hydride intermediate prepared using a monofunctional silane (DMMS) in sc-CO$_2$ displays resonances at −101 ppm and −110 ppm which correlated to siloxane (Q^4) and free silanol groups (Q^3), respectively [33,34]. The relatively low intensity of the Q^3 resonance compared to peak intensity of Q^4 indicates that the amount of residual silanols remaining on the silica surface following silanisation in sc-CO$_2$ is

Table 1
Surface coverage values for silica hydride prepared using dimethylalkoxysilane in organic solvent (dioxane, toluene) or sc-CO$_2$ as reaction medium.

Silica, particle size, pore size, surface area	Silanisation method	% C	Surface coverage (μmol/m^2)[a]
Exsil-Avanti, 3 μm, 130 Å, 205 m^2/g	DMMS silanisation in dioxane[b]	1.2	2.47
Exsil-Avanti, 3 μm, 130 Å, 205 m^2/g	DMMS silanisation in sc-CO$_2$[c]	1.6	3.5
LiChrosorb Si-100, 10 μm, 284 m^2/g	DMES silanisation in toluene[d]	1.47	2.24

[a] Surface coverage calculated using equation derived by Berendsen and deGalan: $\alpha(\mu\text{mol/m}^2) = \frac{[10^6 \cdot (\%C)]}{[(100 \cdot C \cdot n_c \cdot S) - (1 - (\%C/100))]}$.

[b] Reaction mixture refluxed in dioxane at 100 °C for 3 h.

[c] Reaction carried out in supercritical carbon dioxide at 7000 psi, 100 °C for 3 h.

[d] Reference: Lynch et al. [32].

minimal. In addition, there is no direct evidence from the ^{29}Si CP-MAS spectrum of the presence of geminal silanol groups (Q^2) on the surface of the sc-CO_2 generated silica hydride intermediate.

As is evident from ^{29}Si solid state NMR spectroscopic studies, the low amount of residual silanols remaining after silanisation point to a high conversion efficiency of surface silanols to silica hydride functionality following silanisation in sc-CO_2. These findings are consistent with the percent conversion efficiencies of surface silanols to silica hydride groups as determined from elemental analysis.

The ^{13}C CP-MAS NMR spectrum of the monofunctionally prepared silica hydride intermediate showed an intense peak at −2 ppm corresponds to the equivalent methyl groups of the main M_H species which was observed in the ^{29}Si CP-MAS NMR spectrum, which is again consistent with a silanisation reaction involving a monofunctional reagent.

3.2.2. ^{29}Si and ^{13}C CP-MAS NMR investigations of trifunctionally prepared silica hydride intermediate

The sc-CO_2 preparation of a silica hydride intermediate was also investigated with the reaction of Exsil-Avanti 3.0 μm porous silica particles with a trifunctional silane, triethoxysilane (TES) under supercritical fluid conditions of 120 °C, 483 bar and a reaction time of 3 h. Optimisation studies for the preparation of the TES silica hydride confirmed the use of the same reaction conditions. Surface coverages cannot be accurately calculated using the equations derived by Berendsen and de Galan for the silica hydride intermediate prepared from a trifunctional reagent [9,34]. Reactions involving multifunctional silanes (di-, trifunctional) differ from monomeric phases in that more than one linkage to the silica surface is possible. The use of this surface coverage calculation is therefore hindered by the unknown contributions of the various organosilane species to the number of carbon atoms per anchored organic ligand (n_c) in the equation.

Chu and Pesek previously utilised ^{29}Si CP-MAS NMR spectroscopy to quantify the surface coverage of a silica hydride intermediate prepared by the controlled chemisorption of silanetriol, $HSi(OH)_3$, the hydrolysis product of a trisubstituted silane on a silica surface [24]. Silica hydride conversion efficiencies can be calculated by measuring the areas (half peak width by peak height) of the silica hydride silicon species peaks (resonances observed between −74 ppm and −84 ppm) with respect to the total area of all peaks excluding the area of the Q^4 (siloxane) resonance. Thus, the conversion efficiency can be determined as follows:

%Efficiency

$$= \frac{(\text{Area of hydride})}{(\text{Total area of hydride} + \text{free silanols} (Q^3) - \text{area of siloxane} (Q^4))}$$

From the ^{29}Si CP-MAS NMR spectrum (Fig. 2(a)) a conversion efficiency of 70% can be estimated for the silica hydride intermediate prepared from triethoxysilane (%C 1.7) in sc-CO_2.

The relatively high conversion efficiency achieved using the trifunctional reagent can possibly be attributed to the negligible steric effects that exist, and also that the silane triol can undergo cross-linking to adjacent silanols. In accordance with the proposed mechanism of organosilanisation, the alkoxy groups of the silane reagent undergo hydrolysis to form silanols. Thus the dimethylmethoxysilane reagent is hydrolysed by trace amounts of water present in the CO_2 employed for these reactions and also on the silica surface, resulting in dimethylsilane which possesses one silanol group. Conversely, the ethoxy groups of the triethoxysilane hydrolyse to form a silane with three silanol groups. Therefore, the monofunctional dimethylsilane reagent is sterically bulkier than the silane triol arising from the trifunctional silane. Hence, the methyl groups of the monofunctional silane may prevent adja-
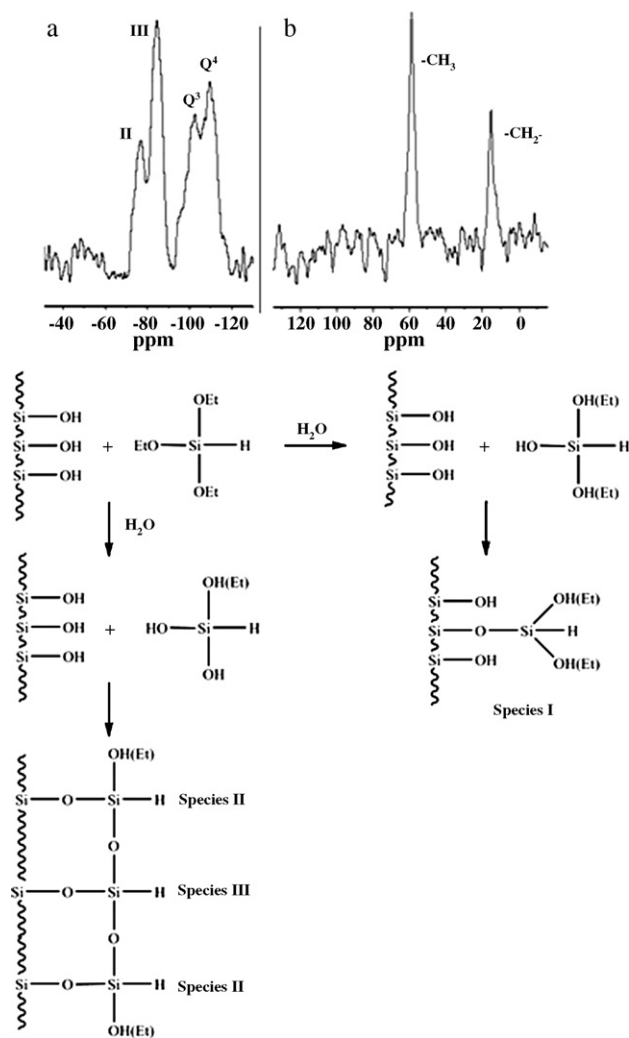

Fig. 2. (a) ^{29}Si CP-MAS NMR spectrum and (b) ^{13}C CP-MAS NMR spectrum of trifunctionally (TES) prepared sc-CO_2 generated silica hydride intermediate; Structure and formation of trifunctionally prepared sc-CO_2 generated silica hydride species.

cent surface silanols from reacting with the hydrolysed silane, thus resulting in a lower surface coverage. The fact that silanol conversion efficiencies are not larger than the available surface silanols suggests that excessive polymerisation did not occur on the surface, thus indicating the formation of a monolayer of hydride groups on the silica surface.

These conversion efficiencies, as determined from spectral analysis, appear superior to those values obtained using organic solvent based methods such as silica chlorination-reduction and TES silanisation in dioxane [24]. However, a comprehensive comparison between silanol conversion efficiencies using TES will require further studies utilizing silica materials of the same physiochemical characteristics. The high silanol conversion efficiency achieved for the TES silanised silica hydride intermediate prepared in sc-CO_2 may be attributed to the higher diffusivity and enhanced mass transfer kinetics of sc-CO_2 compared to organic solvents. In addition, these superior surface coverage values correlate with previous findings which demonstrated that inaccessible silanols are actually accessible in sc-CO_2 compared to organic solvents [9].

The ^{29}Si CP-MAS NMR spectrum of the trifunctionally prepared silica hydride intermediate displays resonances at −74 ppm and −84 ppm which can be assigned to surface hydride surface species II and III, respectively, the structures and formation of which are also shown in Fig. 2.

Surface bound moisture on the native silica and trace water in the CO_2 employed can hydrolyse one or more of the ethoxy groups of the trifunctional silane (TES). These silane silanols condense with silica surface silanols to form covalent linkages to the silica surface. The formation of the silica hydride surface species I results from the hydrolysis of one ethoxy silane group, followed by condensation with one silica surface silanol. The incomplete hydrolysis of the remaining ethoxy groups of this silica species I can be seen from the ^{13}C CP-MAS NMR spectrum of the TES silanised silica hydride intermediate prepared in sc-CO_2 (Fig. 2(b)). However, the hydrolysis of two or more ethoxy groups of the triethoxysilane, results in the formation of silica hydride species II and III. Evidently, crosslinking can also occur, with the condensation reaction of adjacent silanols of covalently attached silanes.

Clearly, the highly crosslinked silica hydride species, III is the predominant species that is formed following TES silanisation in sc-CO_2. There is no evidence from the ^{29}Si CP-MAS NMR spectrum that another possible species denoted as species I was formed as this would appear as a resonance downfield of the other hydride resonances. This silica hydride surface structure (species I) would contribute two additional silanol groups to the silica hydride intermediate surface. Although the silica hydride surface species denoted as II, does possess one silanol group, this does not appear to significantly increase the amount of residual silanols on the silica hydride intermediate surface. This is confirmed by the relatively low intensity of the resonance that is associated with free silanols (Q^3) compared to the Q^4 siloxane resonance (Fig. 2). While further comparative studies on trifunctionally prepared silica hydrides are clearly warranted, the high conversion efficiency of this TES silanisation approach in sc-CO_2 can be contrasted with organic solvent based approaches. Comparing the ^{29}Si CP-MAS NMR spectra of the supercritical and organic solvent based methods, it is clearly evident that the quantity of residual silanols remaining after silanisation is substantially less for the trifunctionally prepared silica hydride intermediate prepared under supercritical conditions.

The ^{13}C CP-MAS-NMR spectrum of the silica hydride intermediate prepared using a trifunctional silane (TES) is shown in Fig. 2(b). Residual ethoxy groups resulting from triethoxysilane silanisation under supercritical conditions correlate to the resonances at 17 ppm and 60 ppm. These peaks can be assigned to the methyl and methylene carbons of these ethoxy groups, respectively. Trace amounts of water arising from the CO_2 utilised and present on the silica surface may not result in complete hydrolysis of the ethoxy groups of triethoxysilane. Therefore, these ethoxy groups may be carried on to the final silica surface species, II and II as shown in Fig. 2.

Both the ^{29}Si and ^{13}C CP-MAS NMR spectra clearly demonstrate the trifunctionally prepared silica hydride intermediate prepared in sc-CO_2 predominantly consists of a highly crosslinked, polymeric type species. The formation of species III and to a lesser extent, species II is consistent with ^{29}Si CP-MAS NMR spectral findings by Chu and Pesek for a silica hydride intermediate prepared via TES silanisation in dioxane [24]. The high conversion efficiency of hydride formation using TES under supercritical conditions is highlighted by the low quantity of free and geminol silanols groups, Q^3 and Q^2, respectively (from the ^{29}Si CP-MAS NMR spectrum) particularly in comparison to the TES silanised silica hydride intermediate prepared using an organic solvent based approach [24].

3.2.3. DRIFT spectroscopy

Evidence of the conversion of surface silanol groups to silica hydride groups can be seen by the distinctive silica hydride (Si–H) stretching vibration at ca. 2260 cm^{-1} as shown in the partial DRIFT curves for the supercritical hydride silica intermediates prepared under supercritical reaction conditions (Fig. 3).
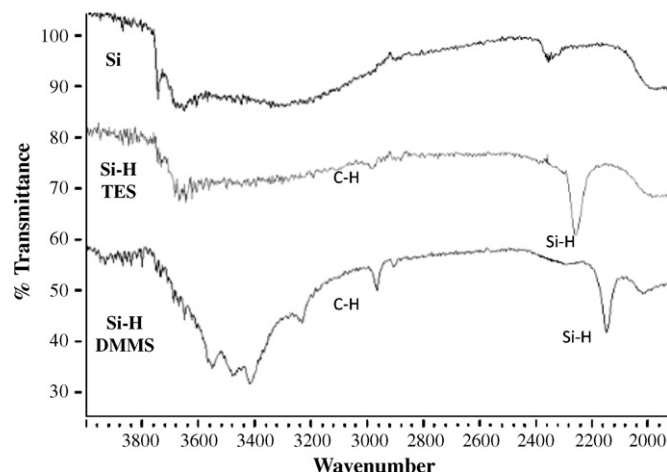

Fig. 3. Partial DRIFT spectral overlay of silica hydride intermediates prepared in sc-CO_2 (100 °C, 483 bar, 3 h): (Si) native, untreated Exsil-Avanti silica; (Si–H, TES) silica hydride prepared using a trifunctional silane (TES); (Si–H, DMMS) silica hydride prepared using a monofunctional silane (DMMS).

The strong stretching band at 2261 cm^{-1} for the silica hydride prepared using triethoxysilane in sc-CO_2 (spectrum (Si–H, TES) in Fig. 3) agrees well with that of a hydride silica prepared by the chlorination-reduction method (2260 cm^{-1}) and also by TES silanisation in an organic solvent (2259 cm^{-1}) [24]. The Si–H stretching vibration for the monomeric silica hydride intermediate (spectrum (Si–H, DMMS) in Fig. 3) is observed at a lower wavelength of 2151 cm^{-1}. The surface structure of this hydride intermediate prepared from a monofunctional silane (DMMS) differs from the surface structure of the hydride silica prepared from the trifunctional reagent (TES) and thus results in a Si–H vibration at a lower wavelength. Indeed, Braun et al. demonstrated that the value of the Si–H stretching vibration is influenced by the number of oxygen bonds, with the stretching frequency increasing with the number of Si–O–Si bonds of the silica hydride species [31].

The stretching band at 2966 cm^{-1}, which is indicative of aliphatic C–H stretching is evident in both spectra of the silica hydride intermediates prepared in sc-CO_2 (spectra (Si–H, TES) and (Si–H, DMMS)), but to a lesser extent for the TES silanised silica hydride (spectrum (Si–H, TES)) as shown in Fig. 3. Conversely, this characteristic stretching peak is absent in the IR spectrum of the native unfunctionalised Exsil-Avanti silica (spectrum (Si) in Fig. 3.). This stretching band at 2966 cm^{-1} corresponds to the equivalent methyl groups of the monofunctionally prepared silica hydride intermediate.

In addition, the intensity of the stretching band at 3739 cm^{-1} due to the O–H stretching of isolated silanols which is present in the spectrum of the native silica, is virtually absent for the silica hydride intermediates prepared in sc-CO_2. This IR feature indicates that hydride preparation using a mono- or trifunctional silane under supercritical conditions does not contribute additional (acidic) isolated silanols to the final silica hydride intermediate. The broad IR absorption between 3620 cm^{-1} and 3200 cm^{-1} can be assigned to bonded silanols (siloxane) groups which are characteristic of the bulk silica [35].

Hence, DRIFT spectral analysis confirms elemental and solid state NMR analysis that an efficient conversion to a silica hydride intermediate was achieved using sc-CO_2 as a reaction medium. The high silanol to silica hydride conversion efficiency of the TES silanisation under supercritical conditions was highlighted by both the intensity of the Si–H stretching band and the absence of the stretching peak associated with isolated silanols.

3.2.4. Thermal analysis of sc-CO$_2$ generated silica hydride intermediate

3.2.4.1. Thermogravimetric analysis (TGA).

Silica surface hydride groups can undergo oxidative degradation to surface hydroxyl groups in the presence of oxygen at temperatures above 350 °C (($Si–H + ½O_2 \rightarrow (Si–OH)$ [22,24]. This exothermic process is accompanied by a weight increase which can be detected by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). A weight increase in the TGA starting at 440 °C and peaking at approximately 550 °C for the trifunctionally prepared silica hydride analysed under oxidising conditions (air) corresponds to the process involving the oxidative degradation of the hydride functionality to surface silanols. This weight gain observed under oxidising (air) TGA conditions confirms the presence of silica hydride species on the silica surface. Evidently, this sample weight gain occurs simultaneously with a general sample weight loss from 80 °C to 800 °C. This weight loss process corresponds to the condensation of silica surface silanols to form siloxanes:

$$2\equiv Si–OH \rightarrow \ \equiv Si–O–Si\equiv \ + \ H_2O$$
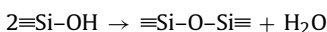
In addition, the general TGA weight loss corresponds to the thermal decomposition of residual ethoxy groups from the silica hydride intermediate surface, the presence of which was indicated by ^{13}C CP-MAS NMR spectroscopy. This general TGA sample weight loss is particularly evident in the TGA curve and first derivative of the sc-CO$_2$ generated silica hydride intermediate which was analysed in inert (N$_2$) TGA conditions. While the observation of this weight gain confirms the presence of silica hydride species for the trifunctionally prepared silica hydride intermediate prepared under supercritical conditions, it does not serve as a satisfactory measure of the extent of silica hydride formation. Chu et al. observed that the relatively rapid decline of the TGA oxidation peak strongly indicates the possibility that the newly formed silanols groups (from the oxidative degradation of silica hydride groups) undergo rapid condensation to form siloxanes [24]. This in turn, hinders the full development of the oxidative degradation TGA peak (evidenced by a weight gain), thus hampering silica hydride quantitation.

3.2.4.2. Differential scanning calorimetry (DSC).

Fig. 4 illustrates the DSC curves analysed under oxidising (air) conditions for the silica hydride intermediates prepared in sc-CO$_2$. The exothermic peaks which occur at 390 °C and 450 °C for the mono-(curve Si–H (DMMS)) and trifunctionally (curve Si–H (TES)) prepared silica hydride intermediates, respectively, result from the oxidative degradation of surface silica hydride groups.

The presence of these DSC peaks confirms the presence of surface silica hydride species. The temperature (450 °C) at which the exothermic peak occurs for the sc-CO$_2$ trifunctionally prepared silica hydride (curve Si–H (TES)) intermediate correlates well with the temperature (460 °C) observed for the silica hydride prepared via TES silanisation using an organic solvent based method [24]. The exothermic peak for the monofunctionally prepared silica hydride intermediate occurs at a slightly lower temperature of 390 °C (curve Si–H (DMMS)), which may be attributed to the differing amount of
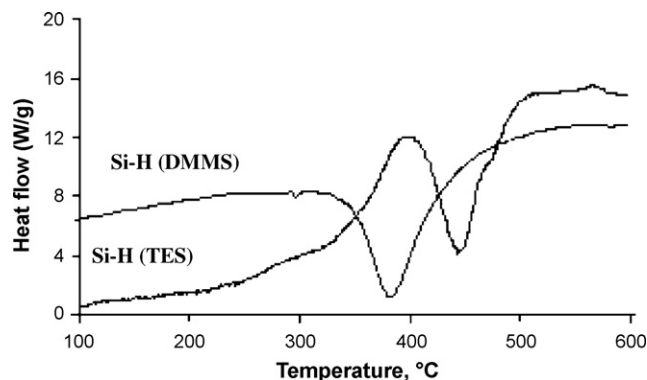

Fig. 4. DSC curves for the thermooxidation of silica hydride intermediates prepared in sc-CO$_2$ run under oxidising conditions (air): (Si–DMMS) silica hydride prepared using a monofunctional reagent; (Si–TES) silica hydride prepared using a trifunctional reagent.

silane linkages that the monofunctional silane can form with the silica surface.

While DSC can be used in conjunction with TGA as a means of confirming the presence silica surface hydride species following silanisation in sc-CO$_2$, DSC is primarily employed to elucidate if excessive polymerisation has occurred. Consequently, these single oxidation peaks for both silica hydride intermediates prepared using a mono- and trifunctional silane indicate that excessive polymerisation did not occur under supercritical conditions.

3.3. Free radical initiated hydrosilation in sc-CO$_2$

This hydrosilation step is typically mediated by an organic or inorganic complex of a transition metal such as platinum, ruthenium or rhodium, of which a solution of hexachloroplatinic acid (H$_2$PtCl$_6$) in 2-propanol, referred to as Speier's catalyst is widely used. Conversely, Pesek and co-workers have demonstrated that a free radical initiator (2,2′-azobis(isobutyronitrile), AIBN) or a peroxide (*tert.* butyl peroxide) can equally facilitate this hydrosilation reaction to generate alkyl bonded LC phases [15]. Hydrosilation is a versatile synthetic process for the attachment of organic moieties to the silica surface, thus generating a wide variety of bonded stationary phases that may not be feasible by other bonding methods.

Heterogenous hydrosilations of octadecene in sc-CO$_2$ via a sc-CO$_2$ generated monofunctionally prepared silica hydride intermediate, and of styrene in sc-CO$_2$ via a sc-CO$_2$ generated trifunctionally prepared silica hydride intermediate are reported here using AIBN. Future research work will examine the effectiveness of various hydrosilation catalysts under supercritical conditions.

As can be seen from examples given in Table 2, an excess of AIBN (from 1.5 to 2.8) was utilised for the octadecene sc-CO$_2$ hydrosilation reactions. AIBN mediated hydrosilation reactions in sc-CO$_2$ (70 °C, 414 bar, 3 h) gave favourable surface coverage values of between 0.8 µmol/m^2 (Si–C$_{18}$-A2) and 3.0 µmol/m^2 (Si–C$_{18}$-A3), dependent on reaction conditions. DRIFT spectroscopy was also utilised to confirm functionalisation in sc-CO$_2$. The chemical bonding of the olefin, octadecene, onto the silica hydride surface

Table 2
Summary of silica hydride (DMMS), octadecene (C$_{18}$) and AIBN (A) quantities utilised for the preparation of a C$_{18}$ silica functionalised silica material via free radical (AIBN) mediated hydrosilation in sc-CO$_2$.

Silica sample	Hydride surface coverage µmol/m^2	Hydride wt. (g)	Cat. wt. (g), mol. Eq.	C$_{18}$ wt. (g) mol. eq.	sc-CO$_2$ conditions	%C	Total surface coverage µmol/m^2
Si–C$_{18}$-A1	3.1	2.5	0.5, 2.0	1.5, 0.4	70 °C/414 bar/3h	9.3	2.4
Si–C$_{18}$-A2	2.4	2.0	0.5, 3.3	4.0, 1.7	70 °C/414 bar/6h	3.5	0.8
Si–C$_{18}$-A3	3.1	3.5	0.5, 1.5	4.7, 0.9	70 °C/414 bar/3 h	12.4	3.0
Si–C$_{18}$-A4	3.1	1.5	0.4, 2.8	2.7, 1.2	70 °C/414 bar/3 h	4.8	1.2

Exsil-Avanti silica particles,
3.0μm, 194m²/g, 120Å

Silanisation → DMMS in sc-CO₂:
100ºC, 414 bar, 3 h

Silica hydride intermediate
%C, 1.4; 3.1μmol/m²

Hydrosilation → AIBN, C₁₈ in sc-CO₂:
70ºC, 414 bar, 3 h

C₁₈ functionalised silica
%C, 9.3; 2.4μmol/m²

Endcapping → HMDS in sc-CO₂:
70ºC, 414 bar, 3 h

Endcapped C₁₈ functionalised silica
%C, 9.4; Total: 2.5μmol/m²

Column packing → Supercritical fluid slurry packing
method in sc-CO₂: 60ºC, up to 345 bar

Packed endcapped C₁₈ LC column
Dimensions: 2.1 mm x 50 mm

Fig. 5. Illustrative schematic of preparation of endcapped C_{18} functionalised packed LC column using sc-CO_2 as a reaction and packing medium.

correlates to a decrease in the intensity of Si–H stretching band at $2150\,cm^{-1}$. In addition, stretching bands between 2800 and $3000\,cm^{-1}$ are characteristic of C–H aliphatic stretches.

3.3.1. Chromatographic performance of endcapped C_{18} functionalised silica material prepared via free radical (AIBN) mediated hydrosilation in sc-CO_2

Supercritical CO_2 also provided the means to endcap the resulting C_{18} bonded phases prepared here, and also an opportunity to utilize the technology to complete the column packing. In this manner, for example, supercritical endcapping with HMDS led to the generation of an endcapped C_{18} phase with a surface coverage of $2.5\,\mu mol/m^2$ (Si–C₁₈-A1; C 9.4%). Furthermore, this supercritical fluid approach was utilised as an alternative solvent free packing method, carried out at $60\,°C$, up to 345 bar. While not yielding in our current investigations, column efficiencies as high as regular solvent slurry packing, a procedure for the elimination of organic solvents, incorporating silanisation, hydrosilation, endcapping and final column packing using supercritical fluid technology has been demonstrated (Fig. 5).

The chromatographic performance of this sc-endcapped C_{18} functionalised silica material was assessed initially using a standard reversed-phase test mixture of benzamide, benzophenone and biphenyl. Theoretical plates of up to 35,000 N/m were obtained for the last eluting solute, biphenyl on this supercritical fluid generated endcapped C_{18} silica material (mobile phase mixture of methanol–water (50:50) at a flow rate of 0.5 ml/min, at $25\,°C$ with an injection volume of 0.1 μl and UV detection at 254 nm). Such column efficiencies are substantially less than theoretical plates achieved for commercially available C_{18} bonded phases (*ca.* 100,000 N/m) prepared using the organic solvent based organosilanisation approach. However, Pesek and colleagues reported column efficiencies of 33,000 N/m (anthracene) on C_{30} silica bonded phase ($1.4\,\mu mol/m^2$) which was prepared using a free radical hydrosilation approach in toluene (either AIBN or *tert.*-butyl peroxide, $100\,°C$, 100 h) [14]. Hence, the column efficiencies obtained for the endcapped C_{18} functionalised silica material prepared and packed under supercritical conditions are comparable to
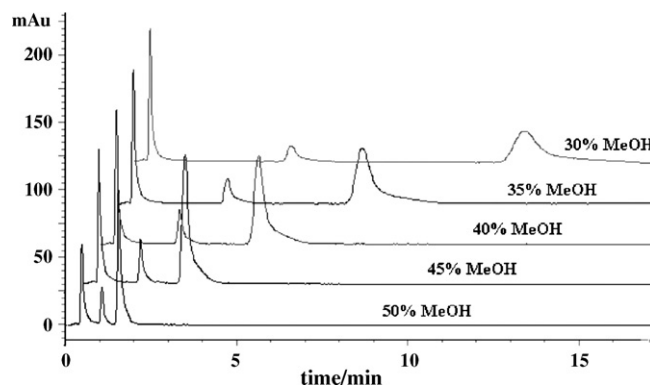

Fig. 6. Chromatogram overlay of variation of percent organic modifier in the mobile phase (methanol) for the separation of benzamide, benzophenone and biphenyl on the sc-endcapped C_{18} stationary phase prepared via AIBN mediated hydrosilation in sc-CO_2. Chromatographic conditions: mobile phase mixture of methanol (MeOH)–water, at a flow rate of 0.5 ml/min, at $25\,°C$ with UV detection at 254 nm.

plate numbers reported for alkyl phases prepared using an organic solvent hydrosilation based approach. Furthermore, the sc-CO_2 hydrosilation method requires a substantially less reaction time (3 h) compared to free radical mediated organic solvent hydrosilation based approaches (100 h).

The variation of percent organic modifier (methanol) in the mobile phase on the retention behaviour of these reversed-phase test solutes gave a linear response with correlation coefficient values (R^2) of 0.982 (benzamide), 0.989 (benzophenone) and 0.989 (biphenyl) (Fig. 6).

3.3.2. Preparation of a phenyl silica stationary phase via hydrosilation in sc-CO_2

As a further example of heterogenous hydrosilation in CO_2, a phenyl stationary phase was prepared by the hydrosilation of styrene in the presence of the free radical initiator (AIBN) on the trifunctionally prepared silica hydride surface under supercritical reaction conditions. The effect of reaction temperature and pressure on the resulting surface coverage (as assessed by TGA and elemental analysis) for this hydrosilation reaction involving styrene was investigated. In general, an overall increase in coverage efficiency was observed under supercritical reaction conditions at the higher temperature and pressure scale of $100\,°C$, 414 bar in a reaction time of 3 h.

Functionalisation of the silica hydride surface with the phenyl functionality via this hydrosilation reaction with styrene in sc-CO_2 was also confirmed using DRIFT spectroscopy. Characteristic vibrations for the phenyl group (aromatic C–H stretching at $\sim 3050\,cm^{-1}$, and bending at 1500 and $1450\,cm^{-1}$) were observed, as well as a significant reduction in the intensity of the hydride characteristic vibration (Si–H stretching at $\sim 2270\,cm^{-1}$) compared to the unreacted silica hydride material. Thermogravimetric analysis of the phenyl functionalised silica material gave a significant weight loss at $430\,°C$. A minor weight loss was observed up to $100\,°C$ which is consistent with physically bound water on the silica surface. Post reaction washing of the phenyl functionalised silica material either with sc-CO_2 or a conventional solvent such as methanol did not reduce this weight loss step observed at $430\,°C$, indicating that all excess reagents have been removed during the synthesis step, indicating chemical functionalisation of the phase. This weight loss step suggests the formation of a chemically bound styrene functionality on the silica surface. A carbon content of 17.4% was obtained for this phenyl functionalised silica phase.

The sc-phenyl silica phase exhibits good separation of a standard test mixture as shown in Fig. 7. The present work demonstrates a
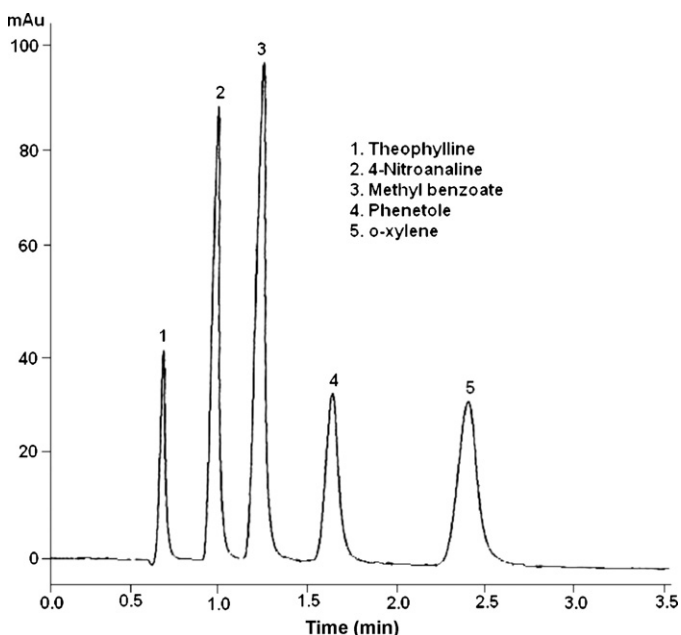
Fig. 7. Separation of test mixture on a sc-phenyl bonded phase (4.6×50 mm, 3 µm), mobile phase composition: 70%/30% H_2O/ACN, flow rate: 1.0 ml/min, temperature ambient (24 °C), pressure: 68 bar and UV detection 254 nm.

novel two-step preparation of a phenyl stationary phase in supercritical carbon dioxide, via a hydride intermediate, without need for post synthesis treatment.

4. Conclusions

Supercritical carbon dioxide has been demonstrated as an efficient reaction medium for the preparation of a silica hydride stationary phase intermediate compared to existing organic solvent based methods. Under supercritical conditions of 120 °C, 483 bar and 3 h, conversion efficiencies of surface silanols to silica hydride functionalities of *ca.* 43% were achieved for the hydride intermediate prepared from a monofunctional silane reagent (DMMS). Silica hydride conversion efficiencies (as determined by ^{29}Si CP-MAS NMR) for the silica hydride intermediate prepared using a trifunctional silane, triethoxysilane in sc-CO_2 were found to be comparable (*ca.* 70%) to those obtained using the TES silanisation approach in an organic solvent (*ca.* 59%). Surface coverages obtained for the supercritical fluid generated hydride intermediate were a two (using a monofunctional silane) to three (using a trifunctional silane) fold increase over those obtained using the chlorination-reduction method.

Solid state NMR analysis also verified that the quantity of residual silanols remaining after supercritical silanisation using both a mono- and a trifunctional silane was not substantial as evidenced from the ratio of geminal silanols (Q^3) to siloxanes (Q^4) groups in the ^{29}Si CP-MAS NMR spectrum. In addition, the amount of residual silanols for the TES silanised silica hydride prepared in sc-CO_2 was considerably less than the hydride material prepared using organic solvent approach, as evidenced by the comparison of the ^{29}Si CP-MAS NMR spectra.

Moreover, DSC analysis confirmed that extensive polymerisation did not occur for the TES silanised silica hydride intermediate, as only single DSC oxidation peaks were observed.

Indeed, the supercritical fluid approach was utilized for all steps in the production of a packed endcapped C_{18} stationary phase, from the preparation of the silica hydride, to the heterogenous hydrosilation, silanol endcapping, to the final column packing. The research described here represents the first example of the preparation of a silica hydride intermediate and subsequent bonded stationary phase preparation via heterogeneous hydrosilation under supercritical fluid reaction conditions, avoiding the use of organic solvents and with a substantially reduced reaction time compared to organic solvent based approaches.

References

[1] L.O. Healy, V.P. Owens, T. O' Mahony, S. Srijaranai, J.D. Holmes, G. Fischer, K. Albert, J.D. Glennon, Anal. Chem. 75 (2003) 5860.
[2] N.M. Scully, L.O. Healy, T. O'Mahony, J.D. Glennon, B. Dietrich, K. Albert, J. Chromatogr. A 1191 (2008) 99.
[3] N.M. Scully, G.P. O'Sullivan, L.O. Healy, J.D. Glennon, B. Dietrich, K. Albert, J. Chromatogr. A 1156 (2007) 68.
[4] G.P. O'Sullivan, N.M. Scully, J.M. Prat, B. Dietrich, V. Friebolin, K. Albert, J.D. Glennon, Anal. Bioanal. Chem. 394 (2009) 1261.
[5] G.P. O'Sullivan, N.M. Scully, J.D. Glennon, Anal. Lett. 43 (2010) 1609.
[6] T. Yarita, T. Ihara, Y. Horimoto, A. Nomura, Anal. Sci. 15 (4) (1999) 377.
[7] M.M. Robson, R. Dmoch, I. Bromilow, K.D. Bartle, P. Myers, High Press. Chem. Eng. 62 (1999) 43.
[8] C. Cao, A.Y. Fadeev, T.J. McCarthy, Langmuir 17 (2001) 757.
[9] B. McCool, C.P. Tripp, J. Phys. Chem. 109 (2003) 8914.
[10] J.R. Combes, L.D. White, C.P. Tripp, Langmuir 15 (1999) 7870.
[11] C.P. Tripp, J.R. Combes, Langmuir 14 (1998) 7348.
[12] W. Gu, C.P. Tripp, Langmuir 22 (2006) 5748.
[13] J.J. Pesek, M.T. Matyska, R.J.J. Yu, J. Chromatogr. A 947 (2002) 195.
[14] J.J. Pesek, M.T. Matyska, E.J. Williamson, M. Evanchic, V. Hazari, K. Konjuh, S. Takhar, R. Tranchina, J. Chromatogr. A 786 (1997) 219.
[15] M.T. Matyska, J.J. Pesek, R. Suryadevara, J. Liq. Chromatogr. Relat. Technol. 28 (2005) 2111.
[16] J.J. Pesek, M.T. Matyska, E.J. Williamsen, R. Tam, Z. Wang, J. Liq. Chromatogr. Relat. Technol. 21 (1998) 2747.
[17] L. Brown, B. Ciccone, J.J. Pesek, M.T. Matyska, Am. Lab. 35 (2003) 23.
[18] J.J. Pesek, M.T. Matyska, S. Gangakhedkar, R. Siddiq, J. Sep. Sci. 29 (2006) 872.
[19] J.J. Pesek, M.T. Matyska, J. Sep. Sci. 32 (2009) 399.
[20] C. Morterra, M.J.D. Low, J. Phys. Chem. 73 (1969) 327.
[21] C. Morterra, M.J.D. Low, J. Phys. Chem. 73 (1969) 321.
[22] J.E. Sandoval, J.J. Pesek, Anal. Chem. 61 (1989) 2067.
[23] J.E. Sandoval, J.J. Pesek, Anal. Chem. 63 (1991) 2634.
[24] C. Chu, E. Jonsson, M.J. Auvinen, J.J. Pesek, J.E. Sandoval, Anal. Chem. 65 (1993) 808.
[25] J.E. Gomez, J.E. Sandoval, Anal. Chem. 82 (17) (2010) 7444.
[26] N. Plumere, B. Speiser, H.A. Mayer, D. Joosten, L. Wesemann, Chem. Eur. J. 4 (15) (2009) 936.
[27] J.F. Brennecke, J.E. Chateauneuf, Chem. Rev. 99 (1999) 433.
[28] C. Aymonier, A. Loppinet-Serani, H. Reverón, Y. Garrabos, F. Cansell, J. Supercrit. Fluids 38 (2) (2006) 242.
[29] G.E. Berendsen, L. deGalan, J. Liq. Chromatogr. 781 (1978) 561.
[30] J.E. Sandoval, J. Chromatogr. A 852 (1999) 375.
[31] M. Braun, K. Nestler, G. Marx, Thermochim. Acta 405 (2003) 73.
[32] B. Lynch, G.H. Müller, L.O. Healy, J.D. Glennon, M. Pursch, K. Albert, Anal. Bioanal. Chem. 377 (2003) 1014.
[33] K. Albert, E. Bayer, J. Chromatogr. 544 (1991) 345.
[34] K. Albert, J. Sep. Sci. 26 (2003) 215.
[35] J. Nawrocki, J. Chromatogr. A 779 (1997) 29.