Preparation and characterization of bonded silica hydride intermediate from triethoxysilane and dimethylmethoxysilane using supercritical carbon dioxide and dioxane as reaction medium

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ABSTRACT

This research examines bonding methodology, surface coverage and silanol conversion efficiencies on the preparation of silica hydride (Si—H) intermediate from triethoxysilane (TES) and dimethylmethoxysilane (DMMS) using sc-CO_2 and dioxane as reaction solvent. Under sc-CO_2 reaction conditions (at temperature and pressure of 100 °C, 414 bar, respectively and 3 h reaction time), the surface coverages of Si—H (evaluated from %C obtained from elemental analysis) prepared with DMMS (3.39 μmol/m^2) and TES (4.46 μmol/m^2) increased by 2- and 4-folds respectively, when compared to reaction performed in dioxane (2.66 μmol/m^2, Si—H, DMMS and 0.69 μmol/m^2, Si—H, TES). The relatively higher surface coverage of Si—H from TES over DMMS generated in sc-CO_2 is due to the inherent trialkoxy moiety of the TES that favours siloxane crosslinkage, forming polymeric surface attachments to yield a higher ligand density than the monomeric DMMS ligand. A conversion efficiency of ~84.4% of Si—H prepared from TES in sc-CO_2 estimated from ^{29}Si CP/MAS NMR analysis is comparable to TES silanization in dioxane or toluene. Moreover, silica hydride (Si—H) conversion efficiency of ca. 42.4% achieved for the hydride intermediate prepared from DMMS in sc-CO_2 is more superior to 33.3% efficiency obtained in dioxane. The differences in conversion efficiencies is attributed to the ability of sc-CO_2 being able to access silica pores that are inaccessible in organic solvents. Bonded silica hydride from TES, DMMS prepared in sc-CO_2 were characterized using elemental analysis, thermogravimetric analysis (TGA), BET surface area, Fourier transform infrared (FI-IR) and solid state NMR spectroscopy. Silica hydride technology/chemical functionalization of silica in sc-CO_2 avoid extended purification steps (i.e. filtration and washing), generation of waste organic solvent and the need of costly or energy consuming drying processing with improved modification efficiency.

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1. Introduction

The catalytic hydrosilation of silicon hydride intermediate via an unsaturated functional group is widely employed to generate hydrolytically stable Si—C linkages. Pioneered by Joseph Pesek, it is now a key synthetic procedure for the preparation of silica bonded phases for liquid chromatography and for the derivatization of capillaries for capillary electrophoresis [1,2]. This two step procedure involved firstly, covalently binding silica hydride moiety to the surface of silica via silanization and secondly coupling of the organic compound terminal olefin to the silicon hydride group in the presence of Speier's catalyst (a 2-propanol solution of hexachloroplatinic acid) [3]. A free radical initiator or a peroxide catalyst provides an alternative to this transition metal catalyst for the preparation of a silica stationary phase [3]. Pesek et al. have demonstrated that careful adjustment of the olefin-catalyst ratio is the key in achieving adequate bonding [4,5].

Silanization/hydrosilation procedure has been used to generate a wide variety of silica hydride stationary phases [2,6–13]. The hydrosilation of alkenes and alkynes has been exploited as a means of introducing a monodentate and bidentate linkage respectively onto a bonded silica phase [9]. Stella et al. reported an approach on how to form a series of stationary phases based on bidentate attachment using a variety of alkyl groups on organosilane reagents [14].

Monterra and Low have demonstrated that the successful conversion of silica silanols to silica hydride is the key to producing an effective silica bonded phase for liquid chromatography [15]. Recently, Pesek et al. have demonstrated the use of silica hydride

in the preparation of fluorinated stationary phases for aqueous normal phase chromatography [10]. It has been shown that the high surface coverage of Si—H using triethoxysilane (TES) as the silanization ligand is due to the small steric effect from the hydride group during the water dependent hydrolysis of the ethoxy groups and the pH dependent silanol condensation [16]. This high coverage will determine the loading of the final bonded stationary phase [8]. Sandoval and Pesek demonstrated that silica hydride group can be introduced onto the surface of silica by the chlorination of silica with thionyl chloride followed by reduction with lithium tetrahydridoaluminate (LiAlH$_4$) [17,18]. However, the disadvantages to this two-step procedure is the use of strictly harsh drying conditions that produces volatile reduction by-products such as sulphur dioxide [19]. Chu and Pesek demonstrated that the silica hydride can be prepared by the reaction of silica surface silanol groups with TES, in the presence of water, hydrochloric acid (HCl) as catalyst and dioxane as solvent, a process refer to as silanization [19]. The outstanding properties of silica hydride in a variety of chromatographic applications and formats in organic solvents have been reviewed by Pesek and Matyska [7,20]. New methods on the preparation of Si—H continue to attract interest [16], including an effective high-temperature chlorination–reduction sequence [21] and sc-CO$_2$ modification of Si—H [13].

Although, the silica hydride approach developed by Pesek et al. [19] has become a key synthetic pathway to silica bonded phases; the approach involves tedious purification steps and generation of waste organic solvent. While the chlorine-reduction procedure reported by Plumere et al. to achieve a high Si—H coverage lead to collapse or lost of micropores due to high temperature involved [21]. The use of sc-CO$_2$ as an alternative reaction solvent, avoiding high temperature, purification steps and drastically eliminating waste solvent generation, with improved modification efficiency will address the environmental threat (green chemistry) posed by traditional method of synthesis [13,22] and prevent collapse of pores as reactions are performed at lower temperatures [22].

Jorge et al. reported two alternative approaches for the synthesis of Si—H based on the so-called "self assembled monolayer" (SAM) concept develop by Sagiv [23]. While Scully et al. have demonstrated the preparation of silica hydride in sc-CO$_2$ which eliminates the use of conventional organic solvents and long analysis time [13].

There has been a rapid growth in interest on the use of supercritical carbon dioxide (sc-CO$_2$) as an environmentally benign solvent for the synthesis of bonded phases over a decade now. Yarita et al. demonstrated a method for endcapping octadecylsilyl (ODS)-silica gel using sc-CO$_2$ as a reaction medium [24]. Myers and co-workers synthesized silica bonded phases with alkoxysilanes in sc-CO$_2$ using an autoclave at 150 °C for 20 h [25], while Sealey et al. reported the derivatization of silica with a polyaminosilane in sc-CO$_2$ at 150 °C and low pressure [26]. Ashu-Arrah et al. exploited the solvating power and transport property of sc-CO$_2$ due to low viscosity and high diffusivity to synthesis mercaptopropyl bonded silica (MPS) intermediate at temperature not far exceeding ambient conditions over shorter reaction time [22]. Holmes and co-workers designed a procedure for the synthesis and swelling of large pore diameter mesoporous silica sphere using sc-CO$_2$ as a reaction solvent [28]. Our research group have used this "green chemistry" approach for the preparation of MPS [22], octedecylsilica and phenyl bonded phase via silica hydride intermediate [13], alkyl and fluorinated alkyl phases [29,30], a chiral bonded phase via mercaptopropyl bonded silica intermediate [31], and for polar-embedded [32], and dendritic phases [33].

Cao et al. have demonstrated that supercritical CO$_2$ will adsorbed moisture from silica while performing silanization thus acting as a desiccant, a feature which differentiate sc-CO$_2$ from conventional organic solvents [34]. Tripp and co-workers have

investigated the reaction of silica with organosilanes in sc-CO$_2$ using infrared techniques [35,36]. McCool and Tripp observed that inaccessible silanol groups are accessible in sc-CO$_2$ [37]. Gu and Tripp highlighted the effectiveness of silica silanization in sc-CO$_2$ by studying the reaction of organosilanes with other metal oxides such as alumina and titania [38].

Chemical functionalization of silica in sc-CO$_2$ offer many advantages over conventional methods, as it is non-toxic and non-flammable, thermodynamically and kinetically stable, environmentally benign, inexpensive and available in high purity. The resulting bonded phase can be obtained from by venting off the sc-CO$_2$ as a gas, whereas conventional methods require filtration, extensive washing and drying which are tedious and labour intensive. Furthermore, reactions in sc-CO$_2$ occur at lower temperature and over shorter reaction time, and the low surface tension enable easy penetration of CO$_2$ and ligand, and prevent collapse of pores [39,40]. This, coupled with easily recycled reaction medium offers a viable green chemistry alternative to organic solvent method of preparation [41,42]. These features permit the direct introduction of the modified material into a chromatographic or spectroscopic system without a further clean up step.

Ashu-Arrah et al. recently demonstrated that sc-CO$_2$ generated MPS prepared with trifunctional alkoxysilane provide high surface coverage and more chemically uniform surface silica species compared to phases prepared with mono- and di-alkoxysilanes [22]. This research investigate bonding methodology, surface coverage and silanol conversion efficiencies on the preparation of silica hydride intermediate in both sc-CO$_2$ and dioxane as reaction solvent using triethoxysilane (TES) and dimethylmethoxysilane (DMMS) on same silica type having same physiochemical properties (Exsil-Pure, 3 μm, 223 m^2/g, 118 Å). The bonded silica hydride intermediates were characterized using elemental analysis, solid state NMR, Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), and BET surface area. Its been demonstrated that polymeric C18 bonded stationary phases prepared using different synthetic route have different chromatographic properties [43].

2. Experimental

2.1. Materials

Porous Exsil-Pure silica particles having particle diameter 3 μm, surface area of 233 m^2/g and pore size of 118 Å was purchased from Alltech/Exmere (Lancashire, UK). Triethoxysilane (TES) and dimethylmethoxysilane (DMMS) were obtained from Fluorochem (Derbyshire, UK). HPLC grade methanol, dioxane and tetrahydrofuran (THF) were obtained from Sigma–Aldrich (Dublin, Ireland). Supercritical carbon dioxide (CO$_2$) cylinder was obtained from Irish Oxygen (Cork, Ireland) with >99.9% CO$_2$ purity with <50 ppmv moisture content and <10 ppmv methanol as modifier [22].

2.2. Instrumentation

Reactions in sc-CO$_2$ were carried out using an Isco model 260D syringe pump (to establish and maintain CO$_2$ pressure) with an external 25 mL stainless steel reaction cell with 0.625 sapphire windows at either end of the reaction cell, 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 (type: NiCr—Ni). 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

Table 1
Elemental analysis values of silica hydride prepared using triethoxysilane (TES) and dimethylmethoxysilane (DMMS) using sc-CO_2 and dioxane as reaction solvent.

Property of silica used	Silanization process	%C, %H
Exsil-Pure silica, 3 μm, 118 Å, 223 m²/g	TES in sc-CO_2, 3 h/100 °C/414 bar	2.05, 0.57
Exsil-Pure silica, 3 μm, 118 Å, 223 m²/g	TES in dioxane, 3 h/100 °C	0.36, 0.33
Exsil-Pure silica, 3 μm, 118 Å, 223 m²/g	DMMS in sc-CO_2, 3 h/100 °C/414 bar	1.70, 0.45
Exsil-Pure silica, 3 μm, 118 Å, 223 m²/g	DMMS in dioxane, 1 h/100 °C	1.26, 0.34
Exsil-Pure silica, 3 μm, 118 Å, 223 m²/g	DMMS in dioxane, 2 h/100 °C	1.32, 0.50
Exsil-Pure silica, 3 μm, 118 Å, 223 m²/g	DMMS in dioxane, 3 h/100 °C	1.47, 0.67

without heating (Midi-MR 1 digital IKAMAG) was purchased from Ika Werke Gmbh & Co. KG (Germany).

Elemental analysis of bonded silica samples were performed by the Micro-analytical Laboratory, Chemistry Department, UCC using a analyzer fully CE 440 elemental automated (Exerter Analytical Inc., North Chelmsford, MA, USA) for the thermal conductivity detection measuring carbon, hydrogen and nitrogen after combustion and reduction and an oxygen flask combustion unit (Intek Services Ltd., Surry, UK) for halides.

BET nitrogen adsorption–desorption isotherms were obtained in the department with a Micromeritics Gemini 2375 Volumetric analyser. The bonded samples were degassed under nitrogen for 5 h at 200 °C to removed any absorbed moisture. Specific surface areas were measured by BET method.

Thermogravimetric analysis (TGA) experiments were performed on a Star^e TGA/DSC instrument (Mettler-Toledo AG, Switzerland). A sample of bonded silica (5–10 mg) was placed on a pre-tared 70 μL alumina sample pan on a balance and the weight recorded. The sample was heated over a temperature range 30–900 °C using a linear gradient at a heating rate of 40 °C/min under an inert nitrogen flow rate of 30 mL/min and analysed using Star^e Excellence software. FT-IR spectra of pure silica and bonded phase were performed on a BioRad model FTS 3000 FT-IR spectrometer (Biorad Laboratories, Cambridge, USA) with a FT-IR attachment (Pike Technologies, USA). KBr was ground to a fine powder using a mortar and pestle. A sample holder (width: 6 mm; depth: 2 mm) was filled with KBr, the surface of which was levelled and subsequently utilized 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 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}.

Solid state ^{29}Si NMR measurements was performed on Bruker ASX 300 and DSX 200 spectrometer (Bruker, Rheinstetten) using cross polarization and magic angle spinning (CP/MAS). The ^{29}Si CP/MAS and ^{13}C CP/MAS were recorded at 59.6 MHz and 75.5 MHz respectively, with a contact time of 5 ms (^{29}Si nucleus) and 3 ms for the ^{13}C and a recycle delay time of 1.5 s and 2 s for ^{29}Si and ^{13}C respectively. Representative samples of ca. 250 mg were spun at 4 kHz using 7 mm double bearing ZrO$_2$ rotors (for ^{13}C: ~80 mg in 4 mm rotors at spinning rate of 10 kHz). The line broadening used was about 30 Hz and the spectral width was about 25 kHz. All chemical shifts were referenced to trimethylsilyl ester of octameric silicate (Q$_8$M$_8$) and glycin respectively. Spectrum processing was performed using Bruker TOPSPIN 2.0 software.

2.3. Synthetic procedure for silica hydride stationary phases

2.3.1. Synthesis of silica hydride intermediate in sc-CO_2 and dioxane

The procedure for preparing silica hydride with TES and DMMS using sc-CO_2 and dioxane as solvents has been described previously [13]. The quantity of silane used was generally a five mole equivalent. For 1.0 g of Exsil-Pure silica, 1.4 g of TES or 0.8 g of DMMS was employed. Silica (1.0 g), a magnetic stirrer bar, and 1.4 g of TES or 0.8 g of DMMS were added into a 25 mL reaction cell, sealed

and wrapped with an electrical heating tape. The magnetic stirrer plate was switched on to ensure gentle agitation of the cell contents (600 ± 2 rpm), which was verified by looking through the sapphire windows at either end of the reaction cell. The temperature of the reaction cell was raised beyond the critical temperature of CO_2 (31.2 °C), when the critical pressure (73.8 bar) was reached. The reaction cell was filled with pressurized CO_2 and the reaction carried out at supercritical reaction conditions of 100 °C, 414 bar for 3 h. Following a reaction time of 3 h, the magnetic stirrer was switched off and the cell content allowed to settle for 20 min, followed by dynamic extraction for ~30 min with 120 mL of fresh sc-CO_2 flushed through the cell at a flow rate of ca. 8 mL/min. The reaction cell was then depressurized, vented, cooled and opened and the bonded materials was removed as a white flowing powder for characterization. Elemental analysis values are illustrated in Table 1.

To compared silica hydride prepared with sc-CO_2 with conventional organic solvent based method, reaction in dioxane were performed in a 3-neck 100 mL round bottom flask under refluxed for 3 h in the case of TES and 1 h, 2 h and 3 h with DMMS at 100 °C respectively, a procedure developed by Chu et al. [19]. 1.0 g of porous silica was placed in a 3 neck 100 mL round bottom flask with 20 mL of dioxane as solvent plus a magnetic stirring bar. Into the mixture was added 1.5 mL of aqueous 2.3 M hydrochloric acid as catalyst, stirred and heated to 70–80 °C for 10 min under refluxed. 9 mL of 0.5 M silane/dioxane solution (1.4 g TES or 0.80 g DMMS dissolved in 9 mL dioxane) was added dropwise over a period of 15–20 min using a funnel. The mixture was maintained under refluxed for 3 h for silanization with TES and 1–3 h for DMMS at 100 °C. After the desired reaction time, the reaction content was allowed to cooled under room temperature, separated by vacuum filtration. The resulting products were washed sequentially with 50 mL portions of 20:80 water:tetrahydrofuran (H$_2$O:THF), THF and methanol (twice with each solvent). The recovered white fine powder were dried overnight in an oven at 120 °C, and characterized by microanalysis. Elemental analysis values of silica hydride due to sc-CO_2 and dioxane modification are illustrated in Table 1.

3. Results and discussion

3.1. Thermogravimetric analysis (TGA)

TGA of silica hydride prepared with TES in sc-CO_2 shows a weight loss between 450 and 550 °C corresponding to the decomposition of the hydride group (Fig. 1). As illustrated in Fig. 1, TGA of Si—H prepared at different reaction time at constant temperature and pressure (100 °C, 414 bar) confirms 3 h as the optimum reaction time to achieved higher carbon loading. This results correlate very well with elemental analysis values obtained for silica hydride prepared with DMMS in dioxane at reaction time of 1–3 h (Table 1). The presence of silica hydride species for Si—H intermediate prepared in sc-CO_2 using TES is confirmed by the weight loss at such a high temperature (450–550 °C) corresponding to the oxidative degradation of the hydride group to surface silanol. The mass loss at ca.130 °C correspond to weakly bound physiosorbed surface water, while the weight loss at

Table 2
Surface coverage of silica hydride intermediate prepared using DMMS and TES in dioxane or toluene and sc-CO_2 as reaction solvents.

Properties of silica used	Silanization process	%C	Surface coverage (μmol/m^2)[a]
Exsil-Pure silica, 3 μm, 118 Å, 223 m^2/g	DMMS in sc-CO_2, 3 h/100 °C, 414 bar	1.70	3.39
Exsil-Pure silica, 3 μm, 118 Å, 223 m^2/g	DMMS in dioxane, 1 h/100 °C	1.26	2.47
Exsil-Pure silica, 3 μm, 118 Å, 223 m^2/g	DMMS in dioxane, 2 h/100 °C	1.32	2.60
Exsil-Pure silica, 3 μm, 118 Å, 223 m^2/g	DMMS in dioxane, 3 h/100 °C	1.35	2.66
LiChrosorb Si-100, 10 μm, 284 m^2/g	DMES in toluene, 24 h, 100 °C	1.47	2.24[b]
Exsil-Pure silica, 3 μm, 118 Å, 223 m^2/g	TES in sc-CO_2, 3 h 100 °C/414 bar	2.05	4.46
Exsil-Avanti silica, 3 μm, 130 Å, 205 m^2/g	TES in sc-CO_2, 3 h 120 °C/483 bar[c]	1.7	–[c]
Exsil-Pure silica, 3 μm, 118 Å, 223 m^2/g	TES in dioxane, 3 h/100 °C	0.36	0.69
Silica Vydac TP 106, 6.5 μm, 100 Å, 106.5 m^2/g	TES in dioxane, 5 h/100 °C[d]	0.30	–[d]

–, values not available.

[a] Surface coverage calculated based on de Galan equation: α (μmol·m^{-2}) $= \frac{10^6 \times \%C}{S_{BET}(100\ Cn_c - \%CM_r)}$

[b] Reference: Lynch et al. [50].

[c] Reference: Scully et al. [13].

[d] Reference: Pesek et al. [1].
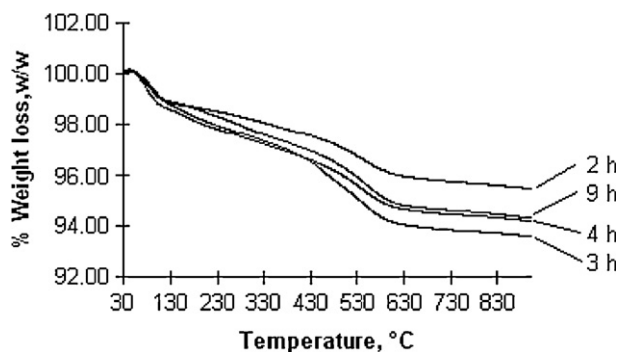
Fig. 1. TGA curves showing effects of reaction time in the preparation of Si—H (TES) in sc-CO_2 at constant temperature and pressure (100 °C, 414 bar).

temperature greater than 650 °C corresponds to the condensation of surface silanols liberating siloxanes and water according to the reaction: $2\equiv$Si—OH $\rightarrow \equiv$Si—O—Si$\equiv$ + H_2O, consistence with recently cited results in literature [22].

The formation of Si—H at relatively fast reaction time is due to three factors: steric effects, electronic inductive effect, high diffusion coefficient and mass transfer kinetics of sc-CO_2 enabling reagents to permeate silica pores which are not accessible in conventional organic methods. The fast reaction rate clearly demonstrate the superior reactivity of Si—H containing alkoxysilanes in sc-CO_2, therefore sc-CO_2 is a better silanization reaction compared to dioxane (or toluene) as evidenced in carbon loading (Table 1) and surface coverage (Table 2). Cao et al. demonstrated that sc-CO_2 is a good solvent for silylation reactions, comparable or better than conventional organic solvents [34].

Chu et al. noted that the rapid decline of hydride peak observed in TGA indicates the possibility that the newly formed silanol functionality from the oxidation degradation of Si—H functionality

TGA and DSC are used to confirmed the presence of silica hydride functionality, TGA and DSC to a greater extend is often used to show if polymerization has taken placed (by observation of more than one weight loss or peak).

3.2. Surface coverage and silanol conversion efficiencies of bonded silica hydride

The surface coverage of silica hydride prepared using DMMS and TES were calculated using %C derived from elemental analysis and applying Berendsen de-Galan equation [46,47]. A surface coverage of 3.39 μmol/m^2 (C, 1.7%) for silica hydride (Table 1) using DMMS in sc-CO_2 corresponding to a conversion efficiency of 42.4% of surface silanols based on a silanol concentration of 8.0 ± 1.0 μmol/m^2 of native silica [48], which is higher than 2.66 μmol/m^2 (C, 1.35%) corresponding to a conversion efficiency of 33.3% obtained in dioxane using same silica type and reaction temperature of 100 °C for 3 h (Table 2). The surface coverage for monomeric phases is limited to 4 μmol/m^2, yielding silanol conversion efficiency of 50% [48], and the immobilized ligands are evenly distributed across silica surface. McCulley reported maximum surface coverage of bonded ligands between 4 and 4.5 μmol/m^2 [49]. Moreover, the surface coverage of Si—H (DMMS) in dioxane (2.66 μmol/m^2, C, 1.35%,) is higher compared to Lynch et al. DMES silanization in toluene (2.24 μmol/m^2, C, 1.47%) after 24 h [50]. The difference in results is due to different physiochemical properties of silica used, e.g. Lynch et al. use LiChrosorb Si-100, 10 μm, 284 m^2/g.

The surface coverage of Si—H prepared with TES in sc-CO_2 evaluated was 4.46 μmol/m^2 (C, 2.05%), and comparable with 4–4.5 μmol/m^2 maximum surface coverage of bonded ligands reported by McCalley [49]. While ^{29}Si CP/MAS NMR spectroscopy, previously used by Chu et al. [19] to determine the surface species of silica hydride prepared by the chemisorption of silanetriol (H—Si(OH)$_3$ was employed for conversion efficiency and applying the equation [13]:

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

undergo condensation to siloxanes, thus preventing the quantitation of silica hydride [19]. An alternative to the quantitative determination of bonded silica intermediate by thermal analysis is differential scanning calorimetry (DSC) as it provide a clear distinction in phase transition of bare silica and Si—H group. The TGA temperature of 450 °C observed for the sc-CO_2 generated silica hydride (Si—H, TES) curve compares well with DSC temperature of 460 °C reported by Scully et al. [13] and also correlate with Si—H, TES prepared using conventional organic based method [19]. Although

The conversion efficiency is then evaluated by measuring the areas (half peak width by peak height) of the silica hydride silicon species (resonances observed between −75 ppm and −85 ppm) with respect to the total area of all peaks and excluding the areas of the Q^4 (siloxane, HO—Si—H) resonance [19] (Fig. 2).

A conversion efficiency of 84.4% estimated from spectral analysis for Si—H, TES is comparable to the 95% efficiency for organic solvent based methods [7,8]. The high conversion efficiency of Si—H (TES) prepared in sc-CO_2 is attributed to three factors: steric effects (i.e. the presence of very small H— substituent favouring
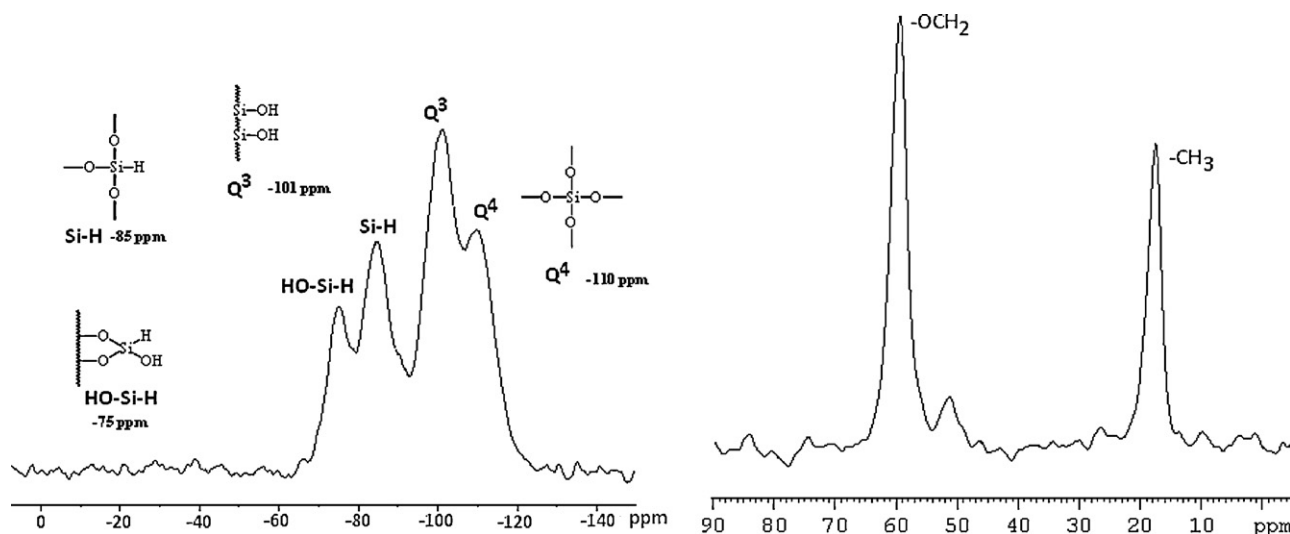
Fig. 2. ^{29}Si CP/MAS NMR spectrum (left) and ^{13}C CP/MAS NMR spectrum (right) of silica hydride (TES) prepared in sc-CO_2.

nucleophilic attack of trace water molecules presence in sc-CO_2 at the center of Si atom form), extensive hydrolysis of the three ethoxy groups ($\equiv$Si—OEt $\rightarrow$ $\equiv$Si—OH + EtOH) and subsequent silanol condensation or cross-linkage ($2\equiv$Si—O—Si$\equiv$ + H_2O) as evidence from ^{29}Si CP/MAS NMR and IR spectra (Figs. 2 and 6 later), coupled with the high diffusivity and enhanced mass transfer kinetics of sc-CO_2 enabling reagent to permeate silica pores that are inaccessible in organic solvents, which is in good agreement with previously reported findings by McCool and Tripp [37].

As illustrated in Table 2, employing sc-CO_2 conditions of 100 °C, 414 bar and 3 h, surface coverage of silica hydride were 2-fold (in DMMS) to 4-fold (in TES) increased using same silica type (Exsil-Pure silica) compared to reaction carried out in dioxane. This is the first example of research work comparing silica hydride prepared from TES and DMMS with silica having the same physiochemical properties (3 μm, 223 m^2/g, 118 Å) using sc-CO_2 and organic solvent based methods. Comparison of silica hydride surface coverage and conversion efficiency cited in literature is usually of silica with different physiochemical properties from different manufacturer. For example, Chu et al. [19] used silica with large particle and pore sizes (Partisil-40, 40 μm, 90 Å, 314 m^2/g) and (Vydac TP (lot 1), 10 μm, 334 Å), while Pesek et al. [1] used Silica Vydac TP 106, 6.5 μm, 100 Å, 106.5 m^2/g, Lynch et al. [50] employed LiChrosorb Si-100, 10 μm, 284 m^2/g. The results presented here using silica type with similar physiochemical properties are further proof reconfirming higher silanol conversion efficiencies using TES and DMMS silanization on silica type of different physiochemical characteristic in sc-CO_2 [13].

3.3. Solid state ^{29}Si and ^{13}C CP/MAS NMR for silica hydride intermediate

3.3.1. ^{29}Si and ^{13}C CP-MAS NMR investigations of Si—H (TES) prepared in sc-CO_2

The advantage of using ^{29}Si CP/MAS solid-state NMR analysis is that they provide information about the species on the surface of silica. The ^{29}Si CP/MAS NMR spectrum of silica hydride prepared with a trifunctional silane (TES) in sc-CO_2 shows resonances at −75 ppm and −85 ppm assigned to the species =HO—Si—H and Si—H, in addition to resonances at −101 ppm and −110 ppm associated to Q^3 (vicinal silanols), and Q^4 (siloxanes) [51,52] respectively, whose reaction mechanism and formation of surface species are illustrated in Fig. 2. The appearance of surface species =HO—Si—H

at −75 ppm is attributed to structural changes occurring on the surface of silica simultaneous to silanization of TES with silanols groups in sc-CO_2. The formation of =HO—Si—H and Si—H is consistence with ^{29}Si CP/MAS NMR spectra results by Chu et al. for silica hydride intermediate prepared through TES silanization in dioxane [19]. The predominant Si—H peak relative to =HO—Si—H is due to extensive hydrolysis of the intermediate species I and subsequent silanol condensation or cross-linkage (Figs. 2 and 3). The relatively high intensity of vicinal silanols Q^3, compared to Q^4 is attributed to the steric hindrance derived from the surface and size of TES reagent preventing approximately half of silanols on silica surface to be converted coupled with incomplete cross-linking thus leading to additional silanol groups being produced which is in agreement with previously cited results in literature [2]. Also, the signal of Q^3 might be due to the influence of internal silanols as observed by Scholten et al. based on deuterium exchange [53]. However, the absent of the most reactive geminal silanols (Q^2, which normally appeared at −92 ppm) on the surface of Si—H as evidenced from ^{29}Si CP/MAS spectrum (Fig. 2) is attributed to high conversion efficiency (4.46 μmol/m^2).

The ^{13}C CP/MAS NMR spectrum of the silica hydride intermediate reveal two peaks corresponding to the bonded organic moiety, i.e. ethoxy group (Si—O—CH_2CH_3). The resonance at 61 ppm represents the methyl carbon atom (C-1) directly bonded to silica (—OCH_2) and the resonance at 17 ppm corresponding to the second methyl carbon (C-2). The low resonance intensity at 51 ppm correspond to the partially hydrolysed residual ethoxy group from species I. This peak as revealed by ^{13}C CP/MAS NMR thus indicate that the terminal groups of Si—H (TES) is essentially made up of ethoxy groups.

As illustrated in Fig. 3, the modification of silica with a trifunctional silane such as TES start with the formation of the intermediate species I [51,54]. In the present of trace amount of moisture in sc-CO_2, extensive hydrolysis of the ethoxy groups ($\equiv$Si—OEt) and subsequent silanol condensation or cross-linkage ($2\equiv$Si—OH $\rightarrow$ $\equiv$Si—O—Si$\equiv$ + H_2O) occurs as well as on the surface of Si—OH groups. The amount of HO—Si—H and Si—H is used as an indirect indicator of the amount of I, since they are generated at the end of the reaction. The more available moisture and solubility of silane reagent in the reaction mixture, the more ethoxy groups of the triethoxysilane are hydrolysed and therefore the larger amount of HO—Si—H and Si—H species are formed with subsequent increased in surface coverage. The reaction mechanism of silica with a
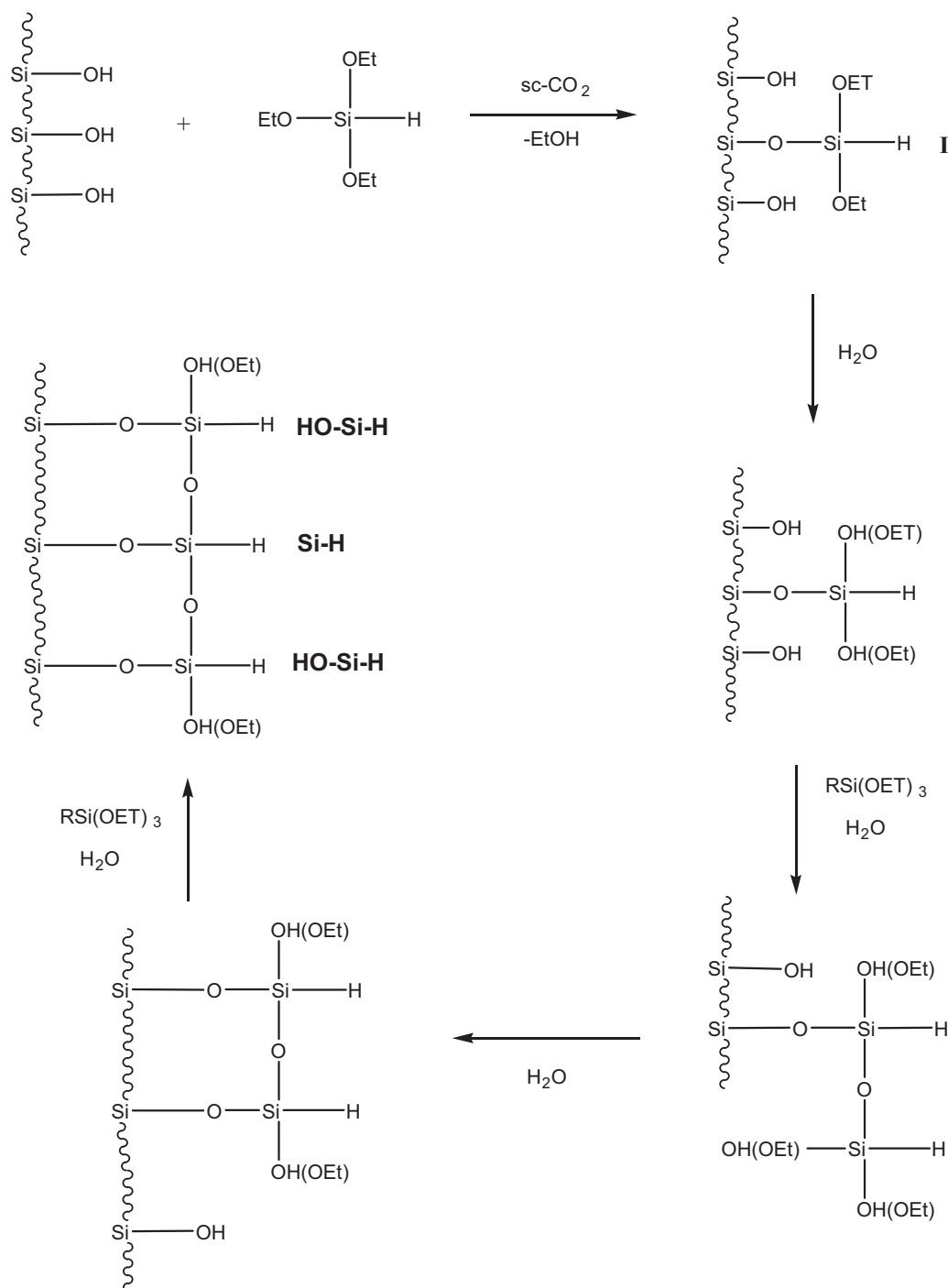
Fig. 3. Reaction mechanism and formation of silica hydride species prepared with TES in sc-CO$_2$ at 100 °C, 414 bar, 3 h.

trisubstituted silane in sc-CO$_2$ and organic solvent has been described by Ashu-Arrah et al. [13,22], Albert et al. [51,54] and Tripp et al. [55,56] respectively.

3.3.2. ^{29}Si and ^{13}C CP/MAS NMR of silica hydride (DMMS) prepared in sc-CO$_2$

^{29}Si CP/MAS NMR spectrum of silica hydride generated using a monofunctional silane such as DMMS reveal an intense single signal of M unit at +14 ppm, showing a consistency with silanization reaction involving a monofunctional reagent, in addition to resonances at −101 ppm (free silanol groups, Q^3) and −110 ppm (siloxane, Q^4) and a small shoulder peak at −92 ppm (geminal silanol, Q^2) corresponding to the parent silica [51,52] (Fig. 4). The high quantity of Q^4 compared to Q^3 is attributed to steric hindrance arising from the surface and size of the DMMS preventing approximately half of the original silanols from silica being covered. This results are in good agreement with recently reported results by Pesek et al. [2]. Scott noted that Q^4 species is hydrophobic and have very little to do with solute retention. However, the relatively low quantity of Q^2 indicate the amount of residual groups left after sc-CO$_2$ silanization is low as evidenced in the high surface coverage (3.39 μmol/m^2).

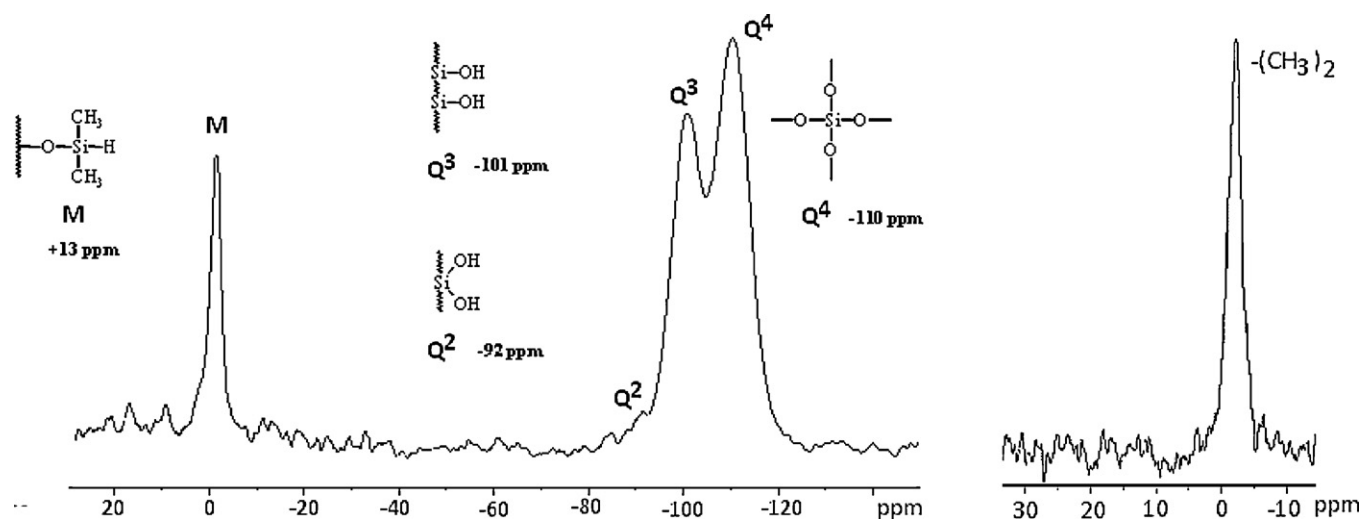**Fig. 4.** ^{29}Si CP/MAS NMR spectrum (left) and ^{13}C CP/MAS NMR spectrum (right) of silica hydride (DMMS) prepared in sc-CO$_2$.

The ^{13}C CP/MAS NMR spectrum of silica hydride (DMMS) in sc-CO$_2$ shows a single intense peak at high-field region at −2 ppm corresponding to the methyl group attached directly to the silica atom (Si−CH$_3$) consistent with silanization reaction using a mono silane.

The formation and structures of the silica hydride due to DMMS silanization in sc-CO$_2$ are shown in Fig. 5 and since the is only one point of attachment, the silanols of the hydrolysed silane reagent condense with silanols on the surface of silica to form a Si−O−Si linkage. Because there is only one hydroxyl group available for bonding, modification of silica with a monofunctional silane is not subjected to extensive hydrolysis and condensation ($f = 1$ for DMMS). Therefore, sc-CO$_2$ (with moisture content <50 ppmv) is a better reaction solvent than organic solvent such as toluene or dioxane for the preparation of stationary phases using monofunctional silanes, as evidence in bonding density (cf. Table 2, C: 1.70%, 3.39 μmol/m^2 vs. C: 1.47%, 2.44 μmol/m^2).

3.3.3. FT-IR spectra of native silica and silica hydride (TES) prepared in sc-CO$_2$

The FT-IR spectra of silica hydride (TES) prepared in sc-CO$_2$ demonstrates successful modification (Fig. 6). The two peaks at ∼2270 cm^{-1} and at 890 cm^{-1} correspond to the hydride characteristic vibration ((≡Si−H), with the adsorption peak at 890 cm^{-1} created during silanization process as a result of cross-linking, absence for naked silica. The υ_{SiH} band at ∼2270 cm^{-1} is in good agreement with the stretching band of Si−H prepared by chlorine-reduction procedure (IR, υ_{SiH} band at 2283 cm^{-1}) [21] and also by TES (Si−H) silanization in conventional organic solvent (IR, υ_{SiH} band at 2250 cm^{-1}) [7]. However, comparing the IR spectra of the sc-CO$_2$ silica hydride (Si−H, TES) and organic based

methods including high-temperature chlorine reduction step, it is clear that extensive cross-linkage occurs as evidence in the υ_{SiH} at two adsorption bands: ∼2270 cm^{-1} and 890 cm^{-1} (Fig. 6) and the amount of residual silanol remaining after supercritical silanization is quite less as evident in the absence of the most reactive Q^2 species (Fig. 2). The peak at 1400 cm^{-1} correspond to weak Si−O vibration for silica and Si−CH$_2$ for silica hydride (Si−H). The appearance of this peak as revealed by FT-IR for silica and Si−H shows that the surface of silica is populated with polar hydroxyl groups (Si−OH) while silica hydride is populated with silicon hydride (Si−H) leaving the surface hydrophobic (Si−OEt) and less polar. As a result, silica hydride do show weak association with water compared to strong affinity of ordinary silica with water. Therefore, a silica surface modification with hydride (Si−H) functionality is desirable as the starting material to formed stable Si−C linkage via heterogeneous hydrosilation with olefin compounds, in the presence of a free radical initiator or Speier's catalyst. The broad peaks around 1300–1000 cm^{-1} are due to production of surface Si−O−Si bond. While the band at 800 cm^{-1} is due to strong Si−O−Si vibration (similar intensity) for silica and silica hydride due to replacement of hydroxyl functionality (Si−OH) by Silicon hydride (Si−H). The adsorption bands at ∼1650 to 1550 cm^{-1} for both silica and silica hydride is due to physisorbed water, and/or bending mode of water in addition to an underlying bulk mode silica surface [27]. The band at 2340 cm^{-1} is due to residual adsorbed CO$_2$ on the surface of silica due to use of sc-CO$_2$, consistence with recently cited results in literature [27,57,58]. The narrow peaks at 3550–3300 cm^{-1} for the two spectra are due to single/geminal hydroxyl and hydrogen bonded hydroxyl groups (O−H), and in good agreement with cited results in literature [36]. The absorptions bands observed at ca. 2950 cm^{-1} are caused by the remaining alkyl groups from

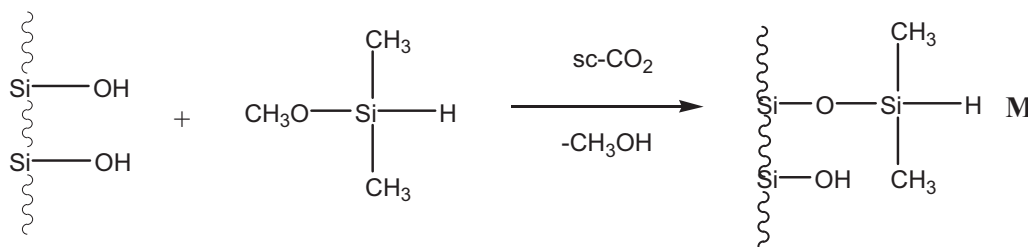**Fig. 5.** Structure and formation of silica hydride species arising from DMMS silanization using sc-CO$_2$ as a solvent.
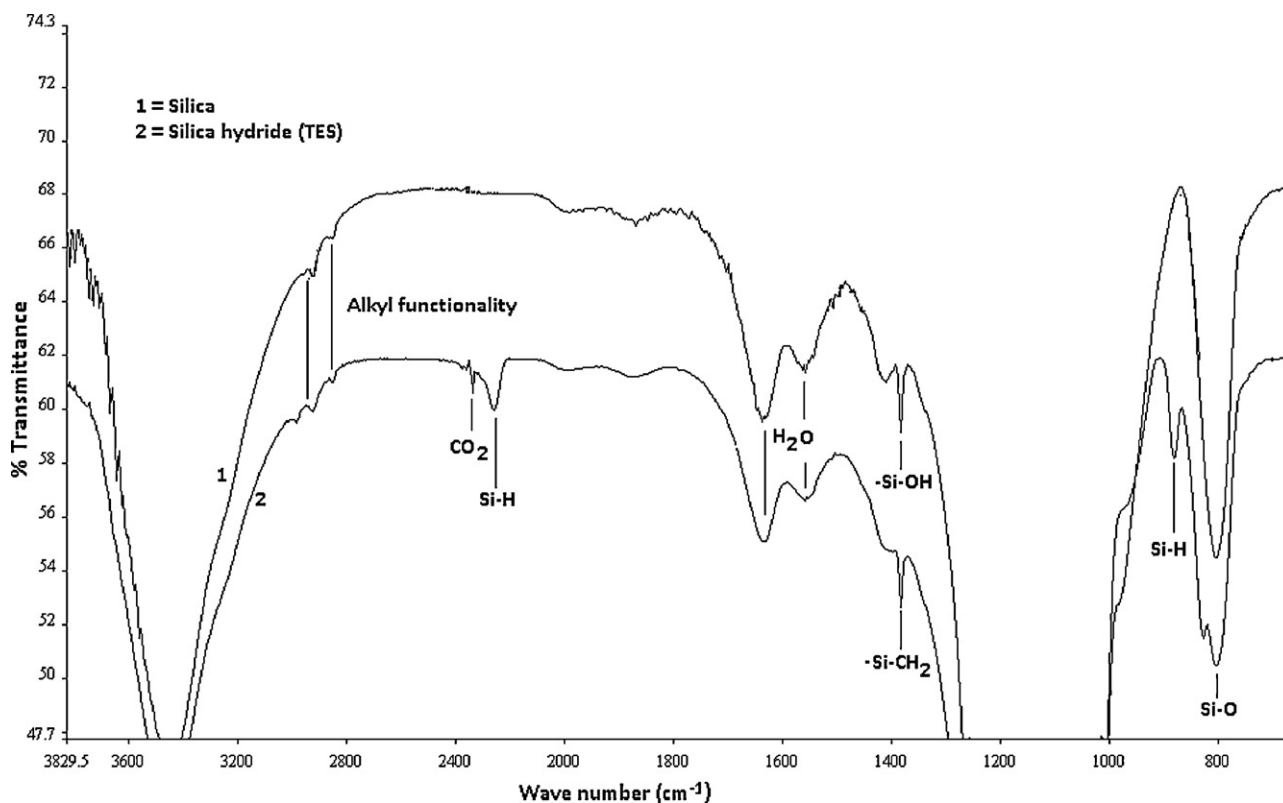
Fig. 6. FT-IR spectrum of silica and silica hydride (TES) generated using sc-CO_2 as a reaction medium.

sol–gel synthesis of the silica and ethyl chain length for silica hydride.

3.3.4. BET surface area, BJH pore size and pore volume analysis

The nitrogen isotherm and pore size distribution curves were used for easy direct visual evaluation of changes caused as a result of the silanization of silica with TES in sc-CO_2 for the generation of silica hydride intermediate phase. As illustrated in Fig. 7, there was no significant decreased in surface area, pore size and pore volume of silica hydride following silanization of silica with TES in sc-CO_2 confirming that polymerization did not occur thus indicating formation of a monolayer of silica hydride functionality on the surface of silica. Moreover, the similarity in BET/BJH surface area, pore size and volume clearly indicate that the monolayer formed

is a complete replacement of hydroxyl groups with hydride functionality, and in good agreement with results cited in literature [22,59].

Also, the shape of the adsorption–desorption isotherms of silica/silica hydride correspond to classification of BET which indicate the characteristic hysteresis of adsorption and desorption typical of mesoporous materials [60]. Three distinct regions are observed: at lower pressures (region a, $P/P_0 = 0.3–0.5$), a linear increase of adsorbed volume with increasing pressure, followed by a sharp increase of adsorbed volume (region b, $P/P_0 = 0.5–0.75$) accompanying by linear increase at higher pressures (region c, $P/P_0 = 0.8$). The three regions are due to a monolayer–multilayer adsorption on pore walls (a) followed by capillary condensation (b) and multilayer adsorption on the outer surface (c) [61]. The slope
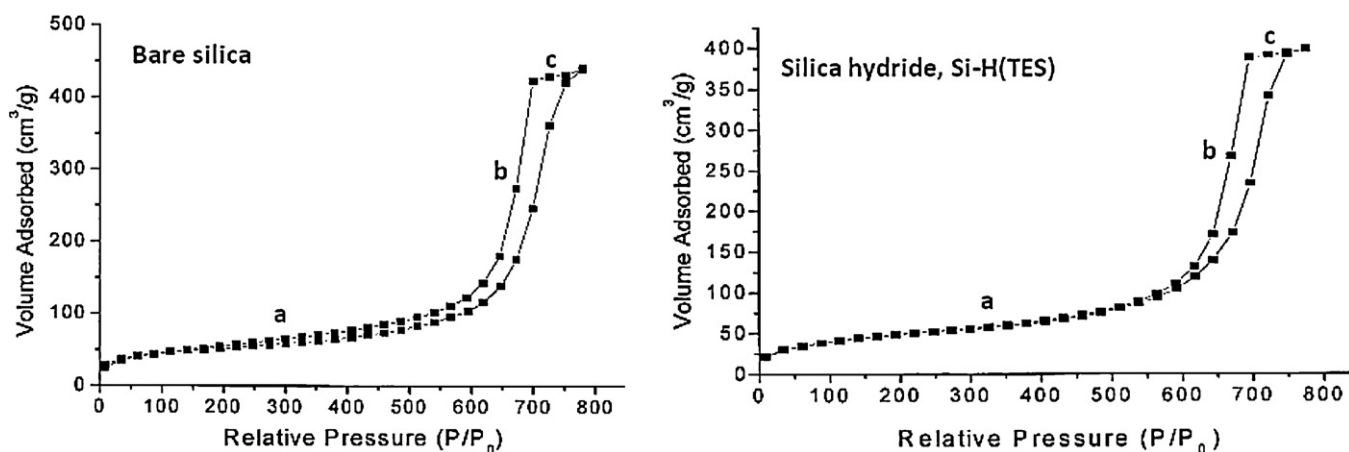

Fig. 7. N_2 adsorption isotherms of silica and silica hydride (Si—H, TES) prepared in sc-CO_2. Filled symbols denote adsorption (below curve) and desorption (above curve). $P/P_0 = 0.05–0.30$ ensuring narrow pore size distribution.

of linear increase at low pressure is slightly larger (region a) for silica hydride than the slope for silica indicating that silica pores are filled with the organic moieties.

4. Conclusions

In this study, it has been demonstrated that sc-CO_2 silanization of silica with TES or DMMS is a viable green chemistry alternative to prepared silica hydride compared to organic based methods. Using sc-CO_2 reaction conditions of 100 °C, 414 bar and 3 h, surface coverage and efficiencies of silica hydride (with respect to silanol groups) with TES (4.46 μmol/m^2) and DMMS (3.39 μmol/m^2) silanization using supercritical CO_2 as solvent are higher compared to conventional organic solvents based methods. Moreover, surface coverage obtained for the sc-CO_2 prepared silica hydride were 2-fold (using DMMS) to 4-fold (using TES) increased compared to dioxane, toluene or high-temperature chlorination-reduction approach. Beside improved surface coverage, the method is simple, environmentally benign, economically cheap and purification step avoided.

Silicon 29 CP/MAS NMR revealed that the amount of residual silanol groups left after sc-CO_2 silanization using both a mono- or tri-functional silane were fewer as evidenced from the ratio of free silanols (Q^3) to siloxanes (Q^4) groups in addition to the absent of the most active Q^2 group. Moreover, the amount of residual silanol groups for silica hydride prepared in sc-CO_2 with TES is considerably less than the hydride intermediate prepared using conventional based method and the high temperature chlorine-reduction sequence, as evidenced in the IR spectra, with Si—H peak adsorbing at two different wave numbers ($\sim$2270 cm^{-1} and 890 cm^{-1}) attributed to high cross-linkage and surface attachment. In addition, there was no significant decreased in pore size and/or collapse in pores of silica hydride following TES silanization with silica (evidence from BET/BJH) confirming polymerization did not take place, coupled with only one weight loss observed in the TGA curve.

The preparation of silica hydride via conventional organic synthetic route [19] or high-temperature (i.e. 900 °C) chlorination-reduction approach [21] involves tedious purification procedures and generation of waste organic solvent. The use of sc-CO_2 as an alternative reaction solvent avoiding purification steps, waste solvent generation and reaction temperatures not far exceeding ambient conditions with improved modification efficiency is advantageous from environmental point (green chemistry) and economic benefits (save energy) [22].

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