Synthesis and characterisation of bonded mercaptopropyl silica intermediate stationary phases prepared using multifunctional alkoxysilanes in supercritical carbon dioxide as a reaction solvent

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ABSTRACT

This research employed ^{29}Si and ^{13}C Cross-Polarisation/Magic Angle Spinning (CP/MAS) NMR spectroscopy to characterise the nature and amount of surface species of di-and trifunctional mercaptopropylsilane (MPS) bonded silica using supercritical carbon dioxide (sc-CO_2) as a reaction solvent without additives (co-solvent) or catalysts. The MPS stationary phases were prepared within 1 h at a temperature and pressure of 70 °C and 414 bar, respectively. Complementary analysis including elemental analysis, thermogravimetric analysis (TGA), DRIFT spectroscopy and BET surface area measurements were employed to characterise the bonded MPS intermediate stationary phases in support of data obtained from solid-state NMR analysis. The results revealed that modification of silica with a trimethoxymercaptopropylsilane (MPTMS) results in ligand surface coverage that is larger than when dimethoxymethylmercaptopropylsilane (MPDMMS) is employed as a silanisation reagent. This observation is attributed to greater reactivity and cross-linkage of trifunctional silane. Reaction in sc-CO_2 in comparison to reflux in organic solvents, is rapid, reducing product recovery procedures.

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1. Introduction

While stationary phases consisting of bare (naked) silica are used for normal phase and/or HILIC chromatography, bonded silica phases prepared using mono-, di- or trifunctional silanes [1–4] are widely used. Elucidating the nature of the resulting bonded stationary phase structures on the silica surface is vital to predict and explain important separation mechanisms in LC. Solid state NMR provides a versatile analytical technique to characterise the bonded species/ligand on the silica surface. For example, ^{29}Si and ^{13}C CP/MAS NMR spectroscopy can distinguish the different Si—O—Si surface species and the dynamic properties of C—C bonds alkyl chains present at the interface of silica support and the bonded ligand by careful assignment of silicon and carbon resonances [2–4].

Water has a significant influence on the reaction of silane ligands on silica surfaces, influencing the ligand surface coverage and species [2,5–7]. The resulting bonded stationary phase density obtained from multifunctional silane (di-, trifunctional) reactions with silica differ from monomeric phases; in the former, more than one linkage of siloxane attachment to a highly crosslinked siloxane between silanes and silica silanols are found [2]. Stationary phases prepared by bonding monofunctional silane to silica surface give a ^{29}Si CP–MAS NMR single resonance peak centered at +13 ppm (M_H) corresponding to ≡Si—O—Si≡ bond. Similar silicon NMR spectra of di-functional modified silica surface give resonances between −4 and −22 ppm of the silane, and trifunctional modified silica will have resonances of T^1 (−46 ppm), $T^{1'}$ (−50 ppm), T^2 (−56 ppm), $T^3 + T^{3'}$ (−59 ppm) in addition to signals at −92 ppm (Q^2, geminal silanol groups), −101 ppm (Q^3, free silanols groups) and −110 ppm (Q^4, siloxanes groups) [2–4].

Albert et al. have studied the reaction mechanism of mono, di-and trifunctional silane with silica under argon atmosphere in organic solvent [2,3]. The type of di-and trifunctional ligand used in silanisation influences the reaction mechanism and the corresponding type and quantitative amount of surface bound species. For example di-and tri-alkoxy silanes are less reactive compared to alkylchlorosilanes [4] and are also less reactive than fluorinated silanes [8,9]. The chlorine atom in chlorosilanes is a better leaving group than the methoxy or ethoxy groups of alkoxysilanes, while the fluorine atom is more electronegative than chlorine atom

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resulting in a different reactivity. The reactivity and condensation of alkoxysilanes are governed by the equation [10,11]:

$$c = \frac{\sum_i i q_i}{f}$$

where q_i is the relative concentration of the $X_{i,j}$ silicon site, obtained by NMR spectrum simulation, i and j is the number of oxo bridges (Si—O—Si bonds) and hydroxyl (OH) groups respectively, f is functionality of precursor (2 for di-, 3 for tri-, and 4 for tetra-alkoxysilanes).

The solubility of silane reagents in reaction media will also affect the formation of surface species (i.e. hydrolysis and condensation). Krasnoslobodtsev and Smirnov have investigated the effect of water on the silanisation of silica wafer with trimethoxysilane (TMS) [6]. Vallant et al. have demonstrated the effect of trace amount of water (present in the reaction media) on the mechanism of surface species, and observed an increase in the quantity of surface species as the trace water content increases [5]. Nieuwenhuyse et al. have shown that the combined use of N-methylacetamide (NMA) and phosphate ions enhances hydrolysis and condensation reaction [12]. Sander and Wise have demonstrated that polymeric C_{18} stationary bonded phases for HPLC prepared using different synthetic pathways have different chromatographic properties [13].

There are trace amount of water present in sc-CO_2, approximately 50 ppmv; in addition, trace amount of methanol is present at approximately 10 ppmv (data obtained from manufacturer). Their concentration is kept low as possible because using a solvent modified CO_2 changes parameter of the mixture [14] e.g. it elevates the critical temperature, so that higher percentage of co-solvent or modifier leads to a subcritical state whose properties are slightly less disadvantageous. This explain why water or methanol is seeded in sc-CO_2 as co-solvents to changed the polarity in order to achieved more selective separation power. The importance of the use of amine catalyst during the silanisation reaction of chlorosilanes and alkoxysilane with silica has been demonstrated [15–17]. Blitz et al. have shown that amines with exchangeable protons are better catalysts than tertiary amine [17]. Tripp et al. have demonstrated that silanisation reaction of silica and chlorosilanes and/or alkoxysilanes requires a catalyst to maximise the yield of surface species [8].

This research seeks to investigate the formation of surface species and coverage of MPS prepared with a di- and trifunctional alkoxysilane using sc-CO_2 as a reaction medium.

Thiol and sulphide groups of mercaptopropyl bonded silica provide a useful reactive site for covalent attachment of ligands via free radical addition [18], disulphide formation [19] and Micheal addition [19,20] for the preparation of polar-embedded stationary phases. Hyum et al. have demonstrated that the polarity induced by MPS bonded phases can enhance steric shielding of the silanol groups on the silica surface [21]. Etienne and Walcarius reported that the hydrophobic property of mercaptopropyl groups on silica surface protected the silica network against degradation in basic conditions [7]. Coman et al. reported characterisation of MPS prepared with 3-mercaptopropyltrimethoxysilane in organic solvent using solid state NMR and FT-IR spectroscopy [22]. Recently Dabre et al. reported use of statistical optimisation to investigate reaction temperature and time in the preparation of a mercaptopropyl silica under reflux in toluene [23].

Yarita et al. demonstrated endcapping of octadecyl silyl (ODS)-silica gels using sc-CO_2 as a silylation medium [24], while Myers et al. reacted silica with alkoxy silanes in supercritical CO_2 using an autoclave at 150 °C for 20 h to generate silica bonded phases [25]. Cao et al. demonstrated that supercritical CO_2 is a good solvent for silylation reactions, comparable or better than organic solvents [26]. Tripp and co-workers have investigated the reaction of silica with organosilanes in sc-CO_2 using infrared techniques [27,28]. McCool and Tripp observed that inaccessible silanol groups are accessible in sc-CO_2 [29]. Gu and Tripp highlighted the effectiveness of silica silanisation in sc-CO_2 by studying the reaction of organosilanes with other metal oxides such as alumina, and titania [30].

However, the current methods of synthesizing stationary phases based on MPS normally involved the use of organic solvents, often creating additional environmental problem of solvent waste disposal. An alternative approach requiring an environmentally benign solvent [31] ("green chemistry") would be desirable.

Supercritical carbon dioxide (sc-CO_2) is a cleaner reaction medium for the modification of silica bonded phases. It has been demonstrated that this "greener" reaction solvent can be employed to synthesise important bonded phases [1], including octadecyl-silica and phenyl bonded phase via silica hydride [32], chiral and polar embedded stationary phase via mercaptopropyl bonded silica intermediate [33,34]. The advantages of using sc-CO_2 as reaction solvent are derived from its non-toxic and non-flammable properties. In addition, sample recovery can be scaled down to simple venting of CO_2, while conventional methods require other time consuming task such as filtration, extensive washing and drying. Furthermore, optimum silanisation reactions carried out in sc-CO_2 at temperatures not far exceeding ambient condition and the reaction time can be relatively short. Using sc-CO_2 as a reaction medium, solvent recycling is simple (via venting) compared to organic solvent methods of preparation [35,36]. sc-CO_2 has no permanent dipole moment and also they possess a low dielectric constant (ca. 1.5) [37,38]. With the exception of the more reactive chlorosilane and most reactive fluorosilane, many organic ligands will show weak solubility in sc-CO_2.

Scully et al. demonstrated that sc-CO_2 generated silica bonded phases prepared with trifunctional silane ligands e.g. trichlorosilanes, provide high ligand densities and more chemically uniform silica surface species compared to the phases prepared with mono- and di-chlorosilanes [1]. This research examines surface species and coverage on mercaptopropyl bonded silica intermediate (MPS) prepared with a di-and trifunctional silane using sc-CO_2 with trace amount of water (<50 ppmv). The bonded MPS phases were comprehensively characterised by elemental analysis, solid-state NMR spectroscopy, DRIFT and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

Exsil-Pure porous silica (particle diameter: 3.0 μm, surface area: 223 m²/g and pore size: 118 Å) and Kromasil silica (particle diameter: 3.5 μm, surface area: 330 m²/g, and pore size: 100 Å) were purchased from Alltech/Exmere (Lancashire, UK). Trimethoxymercaptopropylsilane (MPTMS), and dimethoxymethylmercaptopropysilane (MPDMMS) were purchased from Fluorochem (Derbyshire, UK). Supercritical CO_2 supplied in cylinder was purchased from Irish Oxygen (Cork, Ireland) with >99.9% CO_2 purity with a moisture content <50 ppmv and <10 ppmv methanol as modifier.

2.2. Instrumentation

Reactions were carried out using an ISCO model 260D syringe pump with a 25 ml stainless steel reaction cell (serial no 120773-4, fitted with sapphire windows at both ends), purchased from Thartech Inc. (USA). Teflon coated magnetic stir bar was employed for the stirring mechanism. The temperature was controlled within ±1 °C using an electrical heating tape which made contact with the reaction cell (obtained from Sigma–Aldrich, Ireland). The magnetic

Table 1
Elemental analysis values of MPS prepared with Exsil-Pure (Ex) and Kromasil (Kr) silica using a di-and trifunctional mercaptopropylsilane in sc-CO_2 at 70 °C, 414 bar, 1 h.

Property of silica used	Silanisation process	Bonded phase	%C, %H, %S
Exsil-Pure silica, 3 μm, 118 Å, 223 m²/g	MPTMS silanisation in sc-CO_2	Ex-MPS	2.69, 0.71, 1.81
Exsil-Pure silica, 3 μm, 118 Å, 223 m²/g	MPDMMS silanisation in sc-CO_2	Ex-MPS	2.34, 0.58, 1.64
Kromasil silica, 3.5 μm, 100 Å, 330 m²/g	MPTMS silanisation in sc-CO_2	Kr-MPS	4.08, 0.89, 2.0

stirrer (Midi-MR 1 digital IKAMAG) was purchased from IKA Werke GmbH & Co. KG (Germany).

2.3. Preparation of mercaptopropyl bonded silica intermediate (MPS)

Porous silica (1.5 g) and the mercaptopropylsilane (2.3 g) are charged into the 25 ml stainless steel reaction cell containing a magnetic stirring bar. The cell was wrapped with the electrical heating tape and placed right on top of the magnetic stirrer plate. The reaction cell, filled with CO_2, was heated, via thermal conduction of heat supplied from the electrical heating tape beyond the critical temperature of CO_2 (31.2 °C) when the critical pressure (73.8 bar) was reached. Supercritical reactions were carried out at temperatures of 40 °C, 70 °C, 80 °C, 90 °C and 100 °C, keeping the pressure constant at 414 bar and the initial reaction time was 1 h. Supercritical reactions were also conducted for 3 h, 6 h, and 9 h at temperature and pressure of 70 °C and 414 bar, respectively. Agitation of the cell contents at 600 rpm by the magnetic stirrer ensured that the reactants are properly mixed during reaction. After the desired reaction time, the magnetic stirrer plate was switched off and the cell content allowed to stand for 20 min while still under supercritical conditions. Thereafter the reaction cell was dynamically extracted 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 cell was then depressurised, vented and cooled and the bonded material was removed from the cell for characterisation. Bonded MPS prepared with Exsil-Pure silica is given the notation Ex-MPS and Kromasil silica, Kr_MPS respectively. Elemental analysis values, including %S are given in Table 1.

2.4. Characterisation of bonded MPS generated in sc-CO_2

2.4.1. Percentage carbon
Elemental analysis of bonded MPS phases was performed using the CE 440 elemental analyser (Exerter Analytical Inc., North Chelmsford, Mass, USA) at the Micro-analytical Laboratory, Chemistry Department, UCC (Cork, Ireland).

2.4.2. Thermogravimetric analysis (TGA)
TGA experiments were carried out on a Star^e TGA/DSC instrument (Mettler-Toledo AG, Switzerland). A sample of bonded MPS (5–10 mg) was placed on a pre-tared 70 μl alumina sample pan and the weight recorded. The samples were heated over a temperature range 30–900 °C using a linear gradient programme at a heating rate of 40 °C/min under an inert nitrogen flow rate of 30 ml/min. Data were analysed using Star^e Excellence software.

2.4.3. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy
DRIFT spectra of MPS stationary phases were performed on a Bio-Rad model 3000 FT-IR spectrometer (Biorad Laboratories, Cambridge, USA) with a FT-IR attachment (Pike Technologies, USA). The bonded MPS materials were mixed with KBr at a ratio of 1:30, ground to a fine powder in a mortar and pestle. Pellets of modified samples and KBr (1/10 to 1/15, w/w) of 1 mm thickness were prepared using a hydraulic press. The pellets were placed in a triangular compartment of a FT-IR sample holder. Correction for background absorption was obtained by recording the background

spectrum of KBr. The background spectrum was automatically subtracted from the subsequent spectra of the modified MPS that are run from 4000 cm^{-1} to 400 cm^{-1} at a scan rate of 16 s^{-1} and a resolution of 4 cm^{-1}.

2.4.4. Solid State ^{29}Si and ^{13}C NMR measurements
Solid-state NMR measurement was performed on Bruker ASX 300 and DSX 200 spectrometers (Bruker, Rheinstetten, Germany) using cross polarisation and magic angle spinning (CP/MAS). The ^{13}C CP/MAS and ^{29}Si CP/MAS NMR were recorded at 75.5 MHz and at 59.6 MHz respectively, with a contact time of 3 ms (^{13}C) and 5 ms for the ^{29}Si nucleus, and a recycle delay time of 1 s. Representative samples of ca. 250 mg were spun at 4 kHz using 7 mm double bearing ZrO$_2$ rotors (for ^{13}C: ca. 80 mg in 4 mm rotors at a spinning rate of 10 kHz). The line broadening used was about 30 Hz and the spectral width was about 20 kHz. All chemical shifts were referenced to trimethylsilyl ester of octameric silica (Q$_8$M$_8$) and glycin respectively. Spectrum processing was performed using Bruker TOPSPIN 2.0 software.

2.4.5. BET surface area and BJH pore size and volume
The surface area of the bare silica and the bonded MPS (MPTMS) phases was obtained using the Gemini Micromeritics Tristar II surface area analyser at −196 °C (Glantreo, Cork-Ireland). The samples were degassed under nitrogen for 12 h at 200 °C to expel absorbed gases and moisture.

3. Results and discussion

3.1. Optimisation of sc-CO_2 reaction temperature and time on the preparation of mercaptopropyl bonded silica intermediate

One of the major advantages of supercritical fluids (e.g. sc-CO_2) is that their bulk properties such as solvent density and solvating power can be alter by slight changes in reaction temperature and pressure [39]. Initial investigation of the reaction temperature and time of sc-CO_2 at constant pressure was carried out for the reaction of Exsil-Pure 3.0 μm porous silica particles and trifunctional mercaptopropylsilane (MPTMS). The carbon surface coverage of Ex-MPS (MPTMS) was calculated from data obtained from elemental analysis and from TGA, while the bonding densities for Ex-MPS (MPDMMS) and Kr-MPS (MPTMS) were calculated based on %C derived from elemental analysis, assuming bidentate attachment of bonded silane and applying Berendsen–de-Galan equation [40–42]. The maximum surface coverage for Ex-MPS prepared with MPTMS (Fig. 1(a)) was obtained at reaction conditions performed at 70 °C for 1 h. An observable decrease in surface coverage was found as the temperature and reaction time increases (Fig. 1(b)). Maximum surface coverage of 2.82 μmol/m² and 3.18 μmol/m² was achievable at the optimum reaction conditions (70 °C, 414 bar at 1 h), with the comparable values of bonding densities obtained using CHN and TGA (2.69% vs. 2.99%). The results are in good agreement with those found in the literature [43–45]. The reaction temperature of 70 °C as the optimum for sc-CO_2 preparation of MPS is comparable to what was reported in the literature under organic solvent reaction medium [23]. The surface coverage of Kr-MPS prepared with MPTMS was 3.04 μmol/m², while that of Ex-MPS prepared with MPDMMS was 2.38 μmol/m² (C: 2.34%). The difference in
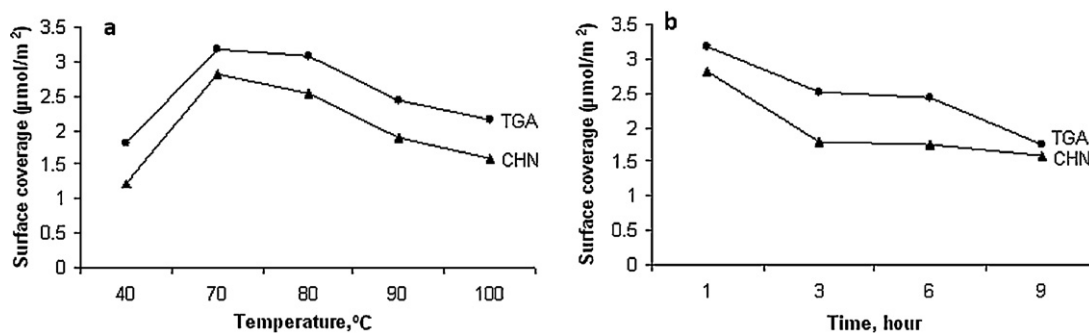
Fig. 1. (a) Effect of reaction temperature (414 bar, 1 h) and (b) effect of reaction time (70 °C, 414 bar) on surface coverage values for Ex-MPS prepared with MPTMS in sc-CO_2.

surface coverage observed for the MPS prepared with Kromasil and Exsil-Pure silica is attributed to the differences in physiochemical property of the silicas (Tables 1 and 2). These results are part of a growing body of evidence which clearly demonstrates the rapid synthesis of bonded silica phases in sc-CO_2 compared to conventional organic solvents which require longer reaction times sometimes days [46].

The use of trifunctional mercaptopropylsilanes does lead to increased surface coverage compared to difunctional mercaptopropylsilane; this is attributed to greater reactivity of trifunctional silane forming both bidentate attachment and siloxane cross-linkages readily to the surface of silica. Higher values of carbon surface coverage (2.82 μmol/m^2 from CHN or 3.18 μmol/m^2 from TGA) and 3.04 μmol/m^2 (Table 2) were achieved from the MPTMS phase prepared in sc-CO_2. These values were relatively larger than those of surface coverage (2.0 μmol/m^2) of MPTMS phase prepared for 28 h reaction time in toluene at 80 °C [18]. Other reports in the literature have shown that lower surface coverage (1.30–1.64 μmol/m^2) of MPTMS can be obtained after 20 h [47]. Although one account has shown that a comparable surface coverage (2.6 μmol/m^2) of MPTMS prepared in toluene can be achieved for a 24 h reaction time [48]. Some reports have also shown that increased carbon surface coverage of 3.9 and 4.2 μmol/m^2 can been achieved from MPTMS bonded silica using reflux toluene [7] [23]. The high surface coverage reported on reflux toluene reaction solvent was enhanced by the addition of tertiary amine catalyst and small amount of water [8,12,15–17]. It is noteworthy that the surface coverages (Table 2) and silica surface species (Figs. 5 and 6 later) observed from the sc-CO_2 reaction here are obtained in a medium with low amount of water <50 ppmv. It is known that

sc-CO_2 can be treated with trace amount of water to improve the reaction of silanes-silica chemistry [49,50] and extraction of metals [37,51].

3.2. Thermogravimetric analysis (TGA/DTG) of sc-generated MPS

From TGA and elemental analysis, supercritical CO_2 generated MPS phases prepared with MPTMS gave higher ligand densities and more chemically bound silica surface species compared to the MPDMMS. The weight loss at 300–430 °C correlates to the decomposition of the MPS phases, while the mass loss at *ca.* 450–630 °C corresponds to the starting material thus confirming presence of thiol species on bonded silica surface (Fig. 2). The weight loss ∼130 °C corresponds to weakly bound surface water while the mass loss at temperature greater >650 °C corresponds to the condensation of surface silanols liberating water and siloxanes according to the reaction: $2 \equiv Si-OH \rightarrow \equiv Si-O-Si \equiv + H_2O$. TGA clearly demonstrates the use of sc-CO_2 as reaction solvent can result in a significant reduction in reaction time and mild conditions for the preparation of MPS (Fig. 2(b)). These advantages merit sc-CO_2 as an alternative reaction solvent for stationary phase preparation to organic solvent refluxing approach which require reaction time for longer hours. The carbon content for Ex-MPS (MPTMS) from TGA was evaluated by a method previously employed by Lumley et al., which involves determining the %C from the weight loss observed at temperature range of 150–600 °C [45]. The small variation in bonding density between CHN and TGA obtained (C: 2.69%, 2.8 μmol/m^2 *vs.* 2.99%, 3.18 μmol/m^2) is due to condensation of silanols at temperature above 630 °C.

Table 2
Surface coverage of MPS prepared with a di-and trifunctional mercaptopropylsilane in sc-CO_2 at 70 °C, 414 bar, 1 h and organic solvent (toluene) as reaction solvent.

Property of silica used	Silanisation process	%C	Surface coverage (μmol/m^2)[a]
Exsil-Pure silica, 3 μm, 118 Å, 223 m^2/g	MPTMS silanisation in sc-CO_2	2.69	2.82
		2.99 (TGA)	3.18
Exsil-Pure silica, 3 μm, 118 Å, 223 m^2/g	MPDMMS silanisation in sc-CO_2	2.34	2.38
Kromasil silica, 3.5 μm, 100 Å, 330 m^2/g	MPTMS silanisation in sc-CO_2	4.08	3.04
Silica (control pore glass CPG) 35–70 μm, 200 Å, *ca.* 300 m^2/g	MPTMS silanisation in toluene, 20 h[b]	–	∼1.30–1.64[b]
Silica (Nucleosil 100-5), 350 m^2/g	MPTMS silanisation in toluene[c]	6.02	2.0[c], 4.62[f]
Silica (Kieselgel Geduran 60, 70 μm)	MPTMS silanisation in toluene[d]	–	3.9[d]
Pharmprep Si 100, 10 μm, 0.81 ml/g, 300 m^2/g	MPDMMS silanisation in toluene 25 h[e]	5.4	4.2[e], 4.39[f]

[a] Surface coverage calc. from Berendsen–de-Galan equation, $\alpha(\mu mol/m^{-2}) = ((10^6 \times \%C)/(S_{BET}(100Cn_c - \%CM)))$.
[b] Reaction under reflux with DMF and imidazole at 100 °C for 20 h [47].
[c] Reaction under reflux with pyridine as catalyst at 80 °C for 28 h [18], surface coverage based on Unger et al. [52] equation, $\alpha_{exp} = ((m(g/g_{silica}))/(M(g/mol) \times S_{BET}(m^2/g)))$.
[d] Reaction under reflux for 24 h [7].
[e] Reaction mixture under reflux with a tertiary amine as catalyst at 75 °C for 25 h [23].
[f] Recalculated value based on Berendsen–de-Galan equation.
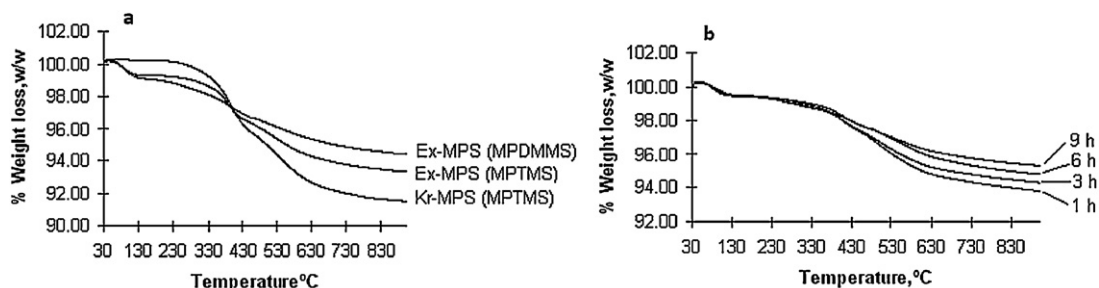–, data not available.

Fig. 2. TGA of (a) MPS prepared with a di-and tri mercaptopropylsilane and (b) effect of different reaction time (70 °C, 414 bar).

3.3. Reaction mechanism of silica functionalisation with MPTMS and MPDMMS in sc-CO_2

3.3.1. Nuclear magnetic resonance spectroscopy (^{13}C and ^{29}Si CP/MAS)

As illustrated in Fig. 3, the silanisation of silica with a trifunctional silane, such as MPTMS starts with the formation of an intermediate **I**.

Hydrolysis of unreacted methoxy groups on the surface bound **I**, in the presence of trace water present in sc-CO_2 leads to the formation of monodentate species T^1. On further reaction with additional silane reagent this monodentate species forms

condensation products T^2 and T^3 species [2,3]. In a similar manner, the functionalisation of silica with the difunctional silane MPDMMS leads to monodentate D^1 and bidentate D^2 ($D^{2'}$) species (Fig. 4). Albert et al. noted that since species T ($T^{1'}$) and D^2 are formed only when the intermediate species **I** is in contact with moisture after silanisation procedure, their formation is an indirect indicator of the amount of intermediate [2,3]. Several authors have also reported similar observations on the effect of water on the modification of silica with silanes [5–7].

^{29}Si CP/MAS NMR analyses clearly distinguish the surface chemistry of the MPTMS and MPDMMS phases prepared in sc-CO_2. As illustrated in Fig. 5(a), the ^{29}Si CP/MAS NMR spectrum of
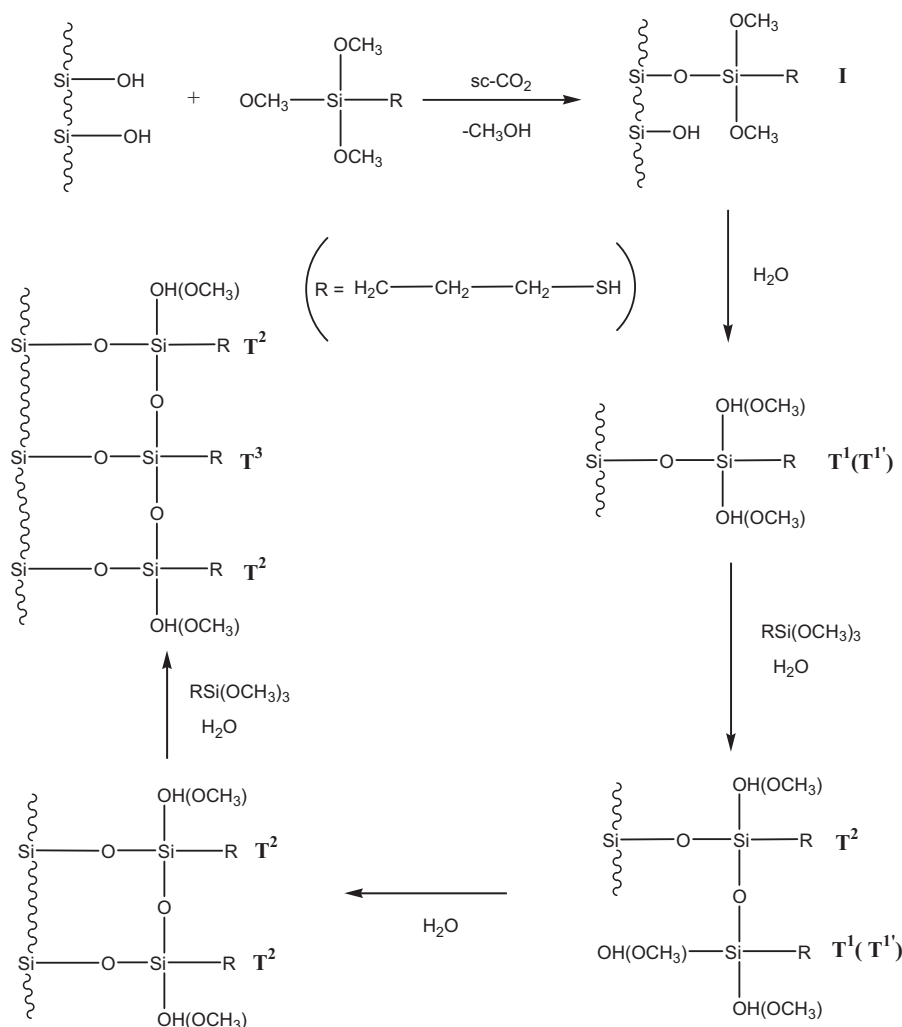

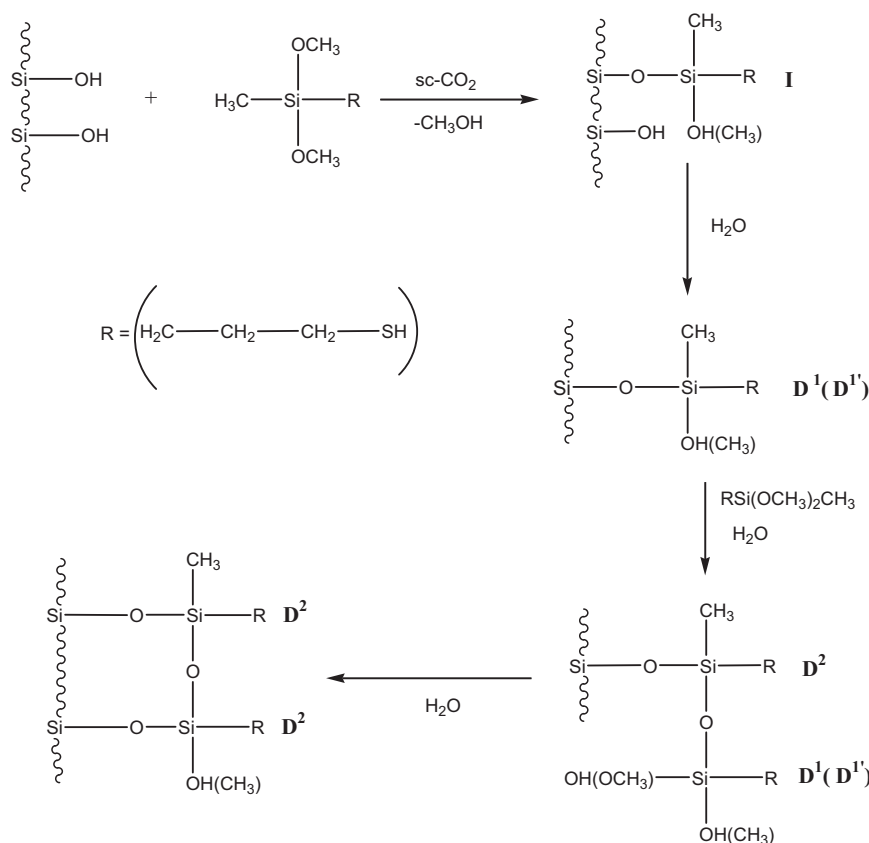**Fig. 3.** Reaction mechanism of MPS and formation of silica surface species for the reaction of silica with MPTMS in sc-CO_2.

Fig. 4. Reaction mechanism of MPS and formation of silica surface species for the reaction of MPDMMS with silica in sc-CO$_2$.

the MPTMS phase displays resonances between -48 ppm (T^1), -56 ppm (T^2) and -65 ppm (T^3), while spectra of MPDMMS phase in Fig. 5(b) reveal resonances at -8 ppm (D^1) and -19 ppm (D^2). The resonances of native silica at -92 ppm (Q^2, geminal silanol groups), -101 ppm (Q^3, free silanols groups) and -110 ppm (Q^4, siloxanes groups) are easily identified on the spectra [2–4]. The low amounts of T^1, T^2 and in particular the highly cross-linked T^3 species (-65 ppm), and of D^1 and D^2 surface species for the bonded MPS prepared in sc-CO$_2$ opens up the need to further investigate the effects of water and reagent solubility in the preparation of silica bonded phases with mono, di and trifunctional alkoxy silanes in sc-CO$_2$. Cao et al. demonstrated that sc-CO$_2$ will adsorbed water from silica while performing silanisation thus acting as a desiccant [26], a feature which distinguishes sc-CO$_2$ from organic solvents. Thus silica bonded phases from organic based synthesis can have higher bonding densities compared to synthesis in unmodified sc-CO$_2$. There is evidence in the literature where water is used as a solvent in chemical reaction and as a reaction partner/or catalyst to increased yield [53]. Albert et al. noted that the more available moisture presence in the modification process, the more favoured is the competition reaction of the intermediate species to hydrolyse and cross-link [2,3]. Etienne and Walcarius noted that the presence of water has a greater influence on silanisation of silica with 3-aminopropyl-triethoxysilane (APES) and mercaptopropyl-ltrimethoxysilane (MPTMS), because water takes part in hydrolysis and leads to increasing silanol condensation [7].

The ^{13}C CP/MAS NMR spectra of MPTMS phases (Fig. 6(a)) show the peak resonance at 12 ppm is assigned to methylene carbon (C-1) directly attached to the silane silicon atom. The intense resonance at 29 ppm is the methylene carbon (C-3) attached directly to the
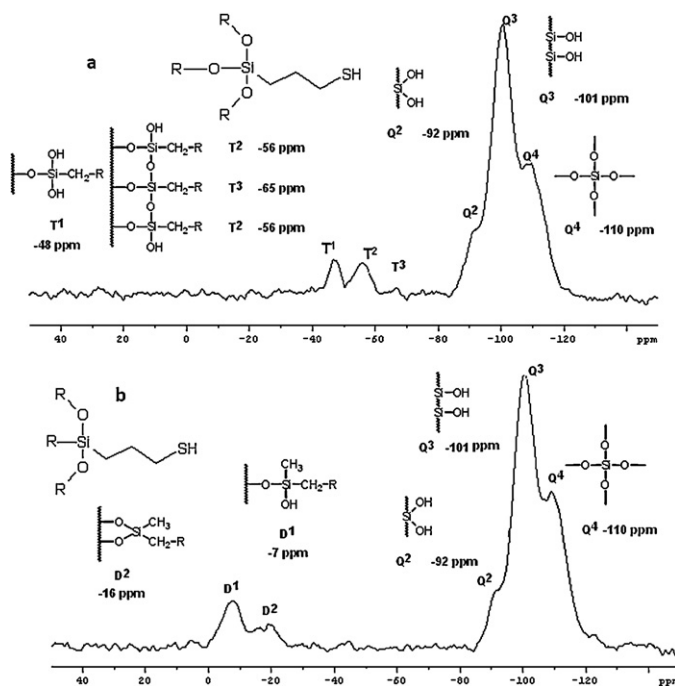

Fig. 5. ^{29}Si CP/MAS NMR spectrum of MPS (a) modified with MPTMS and (b) modified with MPDMMS in sc-CO$_2$.
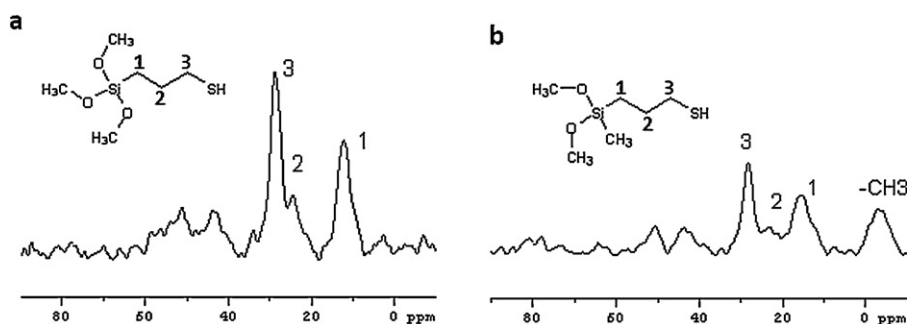
Fig. 6. ^{13}C CP/MAS NMR spectrum of MPS (a) modified with MPTMS and (b) modified with MPDMMS in sc-CO_2.

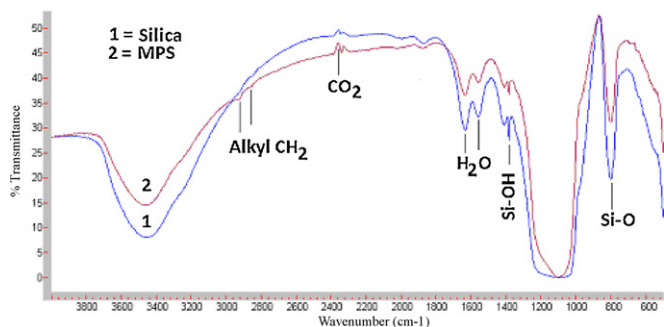**Fig. 7.** DRIFT spectra of silica and MPS prepared in sc-CO_2.

thiol group (−SH), with the shoulder peak at 25 ppm corresponding to the C-2. The ^{13}C CP/MAS NMR spectra of MPDMMS phases (Fig. 6(b)) show similar features as expected, but differing in signal intensities and resolution. These differences are attributed to the lower ligand density evidenced from elemental analysis and TGA. The resonance peak of the propyl alkyl chain at 16 ppm is assigned to carbon atoms at C-1, while the shoulder peak at 23 ppm is assigned to C-2 and the peak at 28 ppm to C-3. The methyl group (−CH$_3$) is assigned to the resonance at ∼0 ppm.

3.4. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy

The DRIFT spectra of MPS (Fig. 7) prepared with MPTMS show weak asymmetry and symmetry vibrations of CH$_2$ at 2930 cm^{-1} and 2860 cm^{-1}. The appearance of low intensity adsorption bands of CH$_2$ is due to the short propyl alkyl chain length. The thiol group (−SH) which normally occurs at 2550–2600 cm^{-1} (wk & shp) is very weak in intensity [54,55]. This weakness in bands intensities is due

to low organic content of ligand on bonded silica surface as evident in %C and ^{1}H–^{29}Si CP–MAS NMR spectroscopy. However, evidence of a successful modification is derived from the appearance of peaks at 2930 cm^{-1} and 2860 cm^{-1}, in addition to a reduction in the intensity of the Si—O—Si adsorption peak between 1386 cm^{-1} and 800 cm^{-1} originally found in silica. The decrease in these peaks is attributed to lower amount of silica probed by IR beam. The two adsorption band at 1600 cm^{-1} and 1560 cm^{-1} is associated with physisorbed water, and/or bending mode of water, in addition to an underlying bulk mode of silica. The peak at 2300 cm^{-1} is due to atmospheric CO_2 and this peak is negative implying it is due to changes in CO_2 in air. Absorbed CO_2 from the use of sc-CO_2 produces a single peak at 2340 cm^{-1} [27,56]. The broad peaks at 3740–3400 cm^{-1} for silica and MPS is due to hydrogen bonded hydroxyl groups [28]. However, the band is not only due to H-bonded silanols as adsorbed water would produce broad peak in this region as well.

3.5. BET surface area and BJH pore size and volume

The nitrogen adsorption isotherm curves were used to show the changes that occur before and after silica modification while adsorption–desorption isotherms were used to calculate mean pore diameters and distributions. BET theory allows for the evaluation of the amount of nitrogen molecules in the dense monolayer (n_m, monolayer capacity) that adsorbed on the measured surface from the experimental adsorption isotherm. As illustrated in Fig. 8, the surface area and pore size of MPS is identical or close to those of silica suggesting no polymerisation which is often observed in conventional organic solvent based methods, while the decreased in surface area indicate silica pore are filled with organic moieties and is in agreement with cited results in literature [44,57].
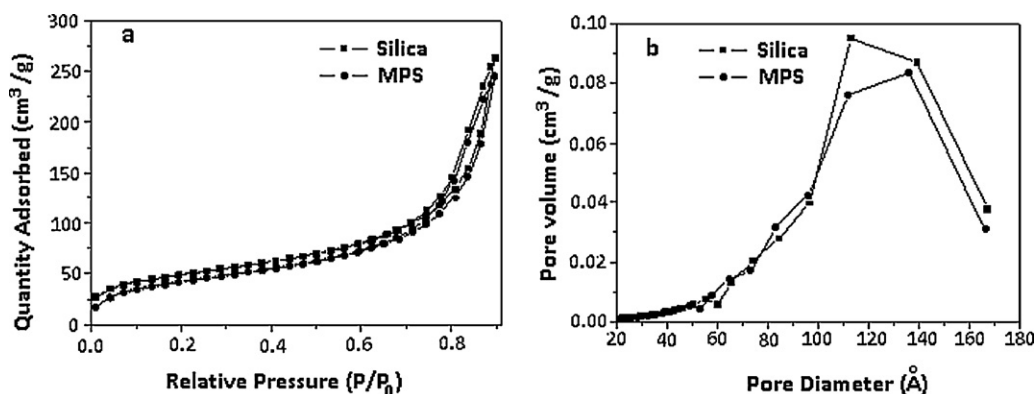

Fig. 8. (a) N$_2$ adsorption and desorption isotherms and (b) pore size distribution curves for silica and MPS (MPTMS) prepared in sc-CO_2.

4. Conclusion

It has been demonstrated that using a di- or trifunctional mercaptopropylsilane, MPS can be rapidly and successfully prepared in sc-CO_2 at reaction conditions of 70 °C, 414 bar for 1 h with reduced workload compared to conventional organic based methods. The tri-functional modified silica with MPTMS gave higher surface coverage evidenced from TGA, ^{29}Si and ^{13}C CP–MAS NMR spectra compared to modification of silica with MPDMMS.

Details concerning the level of partition or distribution of water and adsorbed silanes have not been established quantitatively by the present results and further investigations are warranted. Isolated silanol groups were observed as the major species that governs the primary reaction and adsorption site in silica surface silanols. This finding is in good agreement with previous results based on deuterium exchange reported by Scholten et al. [58] and Chuang et al. [59].

It is anticipated that the utilisation of sc-CO_2 with increased level of water content, can lead to improved coverage of bonded silica stationary phases.

Acknowledgements

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