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Spectroscopic analysis of interactions between alkylated silanes and alumina nanoporous membranes

Jonathan L. Hardin [a], Nathan A. Oyler [b], Erich D. Steinle [a], Gary A. Meints [a,*]

[a] *Department of Chemistry, Missouri State University, 901 S. National Avenue, Springfield, MO 65897, United States*
[b] *Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110, United States*

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ABSTRACT

Transport across alumina nanoporous membranes can be altered via surface attachment of alkylated trimethoxysilane compounds. The mechanism of attachment has been previously assumed to be monolayer silane coverage through full chemisorption regardless of reaction conditions. This chemisorption arises via covalent Si–O–Al bond formation resulting from condensation between the three putative silanols (due to hydrolysis of the three Si–OCH_3 bonds) and hydroxides present on the alumina surface. If this model was correct, methanol would be produced in large quantities in the reaction solution, and the methoxy moieties would no longer be present on the silane molecule. The results presented in this paper utilized FT-IR and both solution and solid-state NMR to examine the chemical nature of octadecyltrimethoxysilane (ODTMS) present on the alumina surface. The FT-IR results confirm the presence of the silane on the membrane. The ^1H solution NMR results indicate small but detectable methanol production during attachment. The solid-state NMR results demonstrate that the methoxy proton NMR integrated peak intensities remain in nearly the same ratios present in the free silane, concluding that the majority of methoxy groups are intact while the silane is attached to the membrane surface. These three results suggest that monolayer surface coverage and chemisorption through full covalent bonding is not the primary means of attachment for ODTMS on the surface of alumina nanomembranes under these reaction conditions.

1. Introduction

Filter membranes made from high purity alumina are utilized in the laboratory as a means of purifying solvents and other solutions. They are synthesized via an electrochemical oxidation of thin aluminum sheets and the size of the pores can be customized to the specific type of filtering required [1]. Commercially, these filter membranes are sold with 20, 100, or 200 nm diameter pores, have uniform pores, high porosity, and large flowrates, and are utilized without further modifications [1–3].

The Martin group became interested in using nanoporous alumina membranes as a means of synthesizing nanotubes of very specific shapes and sizes [4]. This procedure, known as the template method, allows the material of interest to form nanotubes directly within the pores of the alumina membrane. Therefore, the diameters of the nanotubes are correlated to the size of the pore, while the lengths of the nanotubes are dependent on the thickness of the membrane. To date, several different materials, including silica [5], carbon [6], and DNA [7] have been grown as nanotubes using this method.

The usage of silanes to modify inorganic surfaces has been performed extensively [1–3,8–23]. In particular, nanoporous alumina membranes have been modified with alkylated trimethoxysilanes yielding notably different properties than the unmodified membrane [1–3,11,19,21,24]. The modified membranes had significant changes in wetting properties, as water was found to bead on the surface of octadecyltrimethoxysilane-treated membranes [1,2]. Additionally, the transport of permeant molecules through these filter membranes was also altered via the addition of alkylated silanes. Molecular absorbance and fluorescence spectroscopy techniques were utilized to determine the rates of molecular transport through these modified membranes [1,2,11].

Although the properties of the alumina membranes were clearly modified with different alkylated silanes, the exact nature of the attachment to the alumina surface remained unknown. Oxides, primarily SiO_2, Al_2O_3, and other metal/semi-metal oxides, have been modified to yield smooth and treatable surfaces that are amenable for reacting with silanes. These investigations concluded that the silanes directly attach to the oxide surface to form monolayers [24] via the following reaction pathway [3,21,25].

$$\mathrm{RSi(OCH_3)_3} + n\mathrm{H_2O} \rightarrow \mathrm{RSi(OH)}_n\mathrm{(OCH_3)}_{3-n} + n\mathrm{CH_3OH} \qquad (1)$$

$$\mathrm{RSi(OH)}_n\mathrm{(OCH_3)}_{3-n} + \mathrm{HO{-}M}_x\mathrm{O}_y \rightarrow \mathrm{R(OH)}_{n-1}\mathrm{(OCH_3)}_{3-n}$$
$$\mathrm{Si{-}O{-}M}_x\mathrm{O}_y + \mathrm{H_2O} \qquad (2)$$

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[*] Corresponding author. Fax: +1 417 836 5507.
E-mail address: garymeints@missouristate.edu (G.A. Meints).

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Methods of investigating this type of surface modification have included transmission Fourier-transform infrared spectroscopy (FT-IR) [2,10], X-ray photoelectron spectroscopy (XPS) [1], electrochemical current flow and impedance [1,3,9,19], optical ellipsometry [10], time-of-flight secondary-ion mass spectrometry (ToF-SIMS) [19], and molecular absorbance spectroscopy of amino-terminated trimethoxysilanes with a dye [3]. However, these methods have only been able to demonstrate the presence of silanes at the surface. Of these studies, ToF-SIMS [19], XPS [1], transmission FT-IR [2,3], and UV/Vis [11] are the most conclusive that the silanes are present. FT-IR spectra of blank and silane-treated alumina membranes have shown a distinct drop in percent transmission within the 2800–3000 cm^{-1} range for the treated membranes as compared to untreated membranes [2]. ToF-SIMS data indicates evidence of hydrogen bond adsorption of a hydrolyzed trimethoxysilane to the surface of the oxidized alumina membrane [19].

In this work, the nature of the interaction between the alkylated trimethoxysilanes and the alumina nanoporous membrane is examined by utilizing FT-IR spectroscopy along with solution and solid-state nuclear magnetic resonance (NMR) spectroscopy. Examination of the modified membranes directly and of the by-products of the bonding reaction in solution suggests that full covalent chemisorption of the silane to the alumina membrane is unlikely and the silanes may bind via some form of multilayer surface adhesion. FT-IR spectroscopy confirms the presence of the silane on the surface, but offer no insight into the binding mechanism. ^{1}H solution NMR indicates that a small amounts of methanol is being formed under the conditions for silane attachment, as would be expected from Eq. (1), indicating the possibility of some amount of condensation. ^{1}H solid-state NMR (SSNMR) demonstrates the majority of methoxy groups remain intact on the surface of the membrane. These data are consistent with a model of multilayer coverage, where the layer directly interacting with the surface has a single Si–O–Al bond resulting from hydrolysis of one methoxy group, but the remaining methoxy groups remain intact.

2. Experimental

2.1. Reagents

Octadecyltrimethoxysilane (ODTMS), absolute ethanol (EtOH), and tetramethylsilane (TMS) were used as received from Aldrich. A 50 mM sodium acetate buffer was adjusted to pH 5.1 with dilute HCl. Anopore® Anodisc 47 nanoporous alumina membranes with 200 nm diameter pores were obtained from Whatman (Maidstone, England). For solution NMR, chloroform-d and deuterium oxide (D_2O), obtained from Cambridge Isotope Labs (Andover, Massachusetts, USA), were used in an internal coaxial tube for solvent reference and shimming.

2.2. Membrane modification

Membrane modification was accomplished with a two step process, where the membrane is initially pre-treated to remove contaminants followed by the actual silane attachment protocol of Martin et al. [1,11]. Anodized membranes were pre-treated with a dilute HCl/absolute ethanol solution (approximately 7–10 drops of 0.1 M HCl mixed with 2 mL of EtOH). The dilute HCl was added dropwise to cover the membrane. 2 mL of EtOH were added and the entire solution swirled to mix. The membrane remained in this solution for 5 min before removal and was rinsed with EtOH. Once rinsed the pre-treated membrane was placed in a convection oven at 150 °C for 5 min to dry. After being removed and allowed to cool, the membrane was weighed, analyzed via FT-IR and stored in a sealed container until modified.

The methodology for reacting the membranes and ODTMS was adapted from the procedure used by Martin et al. [1,11]. The major procedural alterations include the replacement of aminopropyl trimethoxysilane with ODTMS, allowing the silanization reaction to continue for 30 min, and drying for 30 min. The volumes of reactants used were as follows: 15 mL of absolute ethanol, 2 mL of ODTMS, and 1 mL of 50 mM sodium acetate buffer at pH 5.1. To ensure complete mixing the solution was vortexed for 5 min; which allowed for a more thorough integration given the hydrophobicity of ODTMS. After a thorough rinsing by spraying the modified membrane with 4–5 mL of EtOH to remove any unbound silane, the modified membrane was placed in a convection oven at 150 °C for 30 min to dry.

2.3. FT-IR analysis

Infrared spectra were obtained in the range of 500–4000 cm^{-1} using a Bruker Vortex 70 spectrometer, equipped with OPUS software. Background absorbance data was acquired with a cleaned but otherwise unmodified nanoporous alumina membrane. Membranes that were modified with the silane were then examined separately, while removing the previously acquired background data to eliminate the native absorbance of the alumina membrane. The resulting spectrum is indicative of the presence of any materials remaining on the surface and in the pores of the modified membrane.

2.4. Solution NMR analysis

Solution NMR experiments were performed on a Varian INOVA spectrometer (399.874 MHz proton resonance frequency) with a 5 mm, dual channel auto-x solution probe with pulsed field gradient capabilities. One-pulse ^{1}H and ^{13}C experiments with proton decoupling during acquisition were performed with 8 and 64 transients obtained respectively for each experiment. All ^{1}H and ^{13}C peaks are internally referenced to TMS at 0.00 ppm. All experimental spectra were compared to ^{1}H and ^{13}C spectra of free ODTMS in chloroform-d.

For solution state ^{1}H and ^{13}C NMR the reaction solution was prepared as normal. An aliquot of the appropriate solution was taken and placed in an NMR tube along with TMS for reference. A coaxial tube with D_2O was used for external solvent reference and shimming. Spectra were obtained for the following mixtures: (1) ODTMS/EtOH (15 M EtOH and 0.276 M ODTMS); (2) ODTMS/EtOH/buffer (0.261 M ODTMS, 14.3 M EtOH, 2.78 mM buffer) which had been allowed to react for 30 min; (3) ODTMS/EtOH/buffer/membrane (0.261 M ODTMS, 14.3 M EtOH, 2.78 mM buffer) which had been allowed to react with a membrane present for 30 min. Aliquots of mixtures 1 and 2 were spiked with MeOH to prove full resolution of the methanol peak and the silane methoxy peaks, as well as test the sensitivity of the instrument. Mixture 1 was necessary to prove complete resolution of ethanol and methanol in the presence of ODTMS, without any hydrolysis occurring. Mixtures 2 and 3 are the same as used previously for surface modification and transport alteration [2], and aliquots were taken directly from the modification reaction mixture for solution NMR. For a method known to rapidly produce a sol–gel process, a modified form of the method specified in the work by Fyfe et al. was used [26]. This mixture consisted of the following concentrations: 11.5 M H_2O, 1.31 M ODTMS, 6.03 M EtOH. Also, the chromium acetylacetonate ($Cr(acac)_3$) was not used, as the reported ^{29}Si NMR studies were not performed. The pH was set and held at approximately 2.75 +/- 0.03 via microliter additions of strong acid and base, monitored periodically with a pH electrode. Under these conditions the reacted silanes precipitated out of solution, necessitating filtration to analyze the solutions. This was done via an aspirator vacuum filtration; the solids were rinsed with absolute ethanol.

2.5. Solid-state NMR

For SSNMR, the membranes were modified as stated above. It was determined via gravimetric analysis that a *ca.* 3% mass change occurred during modification, i.e. a 5.7 mg mass change was observed for a 150 mg membrane. This amount of attached ODTMS was typical, and never varied more than ±0.5 mg over multiple trials. Once the membrane was known to have been successfully modified, it was ground in a mortar and pestle and packed into a 3.2 mm SSNMR sample rotor. Additionally, an unmodified membrane was prepared for SSNMR in a similar fashion to act as a control.

All SSNMR experiments were performed on a homebuilt double resonance (HX) SSNMR magic angle spinning (MAS) probe with a 3.2 mm stator from Revolution NMR (www.revolutionnmr.com) on a 8.39 Tesla magnet (357.200 MHz proton resonance frequency) using a Tecmag Apollo console (www.Tecmag.com) configured with a 1 kW Herley 3446 X channel amplifier (www.herley.com) and a 500 W CPC 9T500 M proton amplifier (www.cpcamps.com). MAS spin rates were typically 14 or 16 kHz. ^{27}Al experiments were performed at 93.075 MHz, using a one-pulse, Bloch decay pulse sequence (typical ^{27}Al 90° pulse lengths were 2.4 μs) with 24576 transients. ^{1}H experiments were performed at 357.200 MHz, using a one-pulse Bloch decay or a Bloch decay followed by a four pulse CPMG sequence to remove background signals, with typical 90° and 180° pulse lengths of 2.3 and 4.3 μs respectively. 1024 transients were obtained for the Bloch decay-CPMG background reduced ^{1}H spectrum. All ^{1}H peaks are explicitly externally referenced to TMS at 0.00 ppm. ^{27}Al peaks are referenced to the 1 M $AlCl_3$ at 0.00 ppm via conversion of the proton channel carrier frequency.

3. Results and discussion

3.1. FT-IR Analysis

Infrared spectroscopy has been utilized in prior work to confirm the presence of the substituted silane on the alumina membrane [1]. One of the advantages to this technique is the ability to receive qualitative information about the silanes on the modified alumina surface. Blank (unmodified) membranes were analyzed along with silane-modified membranes. The absorbance spectrum of the blank membrane was then subtracted from the absorbance spectrum of the modified membrane to remove the native absorbance of aluminum oxide. The resulting spectrum is plotted with a spectrum of pure liquid ODTMS ($CH_3(CH_2)_{17}Si(OCH_3)_3$) that was obtained separately (Fig. 1).

Inspection of this data shows similar bands in the 3000–2800 cm^{-1} region, which can be attributed to CH_2 and CH_3 stretches on the octadecyl chain of ODTMS [20]. Unfortunately, this FT-IR data cannot directly indicate the presence of Si–O–Si or Al–O–Si bond linkages, as this region (1100–800 cm^{-1}) is obscured by significant absorbance of alumina (Al–O–Al bonds) [2]. However, this data demonstrates that ODTMS molecules are present on the surface of the alumina membrane.

3.2. Solution NMR analysis

Another approach in analyzing the nature of this attachment reaction is to measure the aqueous products instead of the membrane itself. In the direct attachment reaction depicted in Eq. (1), methanol (CH_3OH) is produced as one or more of the methoxy groups on the trimethoxysilane are replaced with hydroxide from water. Measuring the formation of methanol in the reaction chamber could confirm that this reaction is occurring.

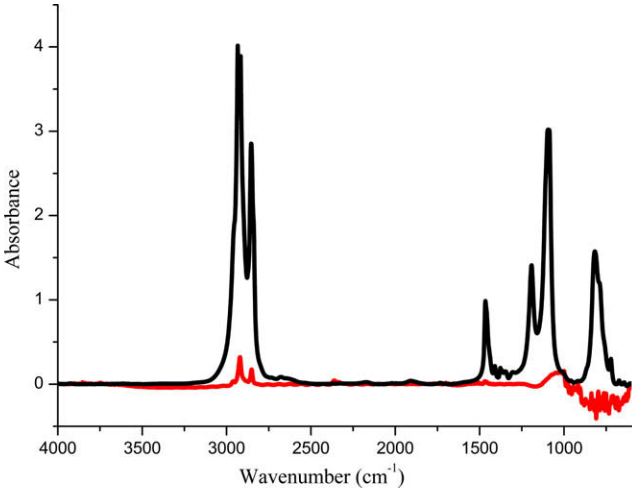

Fig. 1. Overlay of FT-IR spectra from free ODTMS (black) and the modified alumina membrane (red). The peaks in the 3000–2800 cm^{-1} region (attributed to CH_2 and CH_3 stretches) match for both samples, but the region <1500 cm^{-1} (where Al–O–Si bond stretches should occur) is obscured by stretches from the membrane itself (Al–O–Al bonds). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

However, there are other possible reactions that might be taking place between the silane and water. The well-studied sol–gel process [25] involves the complete hydrolysis and condensation of silanes in aqueous solution via the following reactions:

$$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH \tag{3}$$

$$(OH)_3Si{-}OH + HO{-}Si(OH)_3 \rightarrow (OH)_3Si{-}O{-}Si(OH)_3 + H_2O \tag{4}$$

Incomplete hydrolysis leads to a similar reaction pathway with one or more of the –OR groups still remaining. For the current work this would lead to the production of methanol during the hydrolysis and/or the condensation phase(s) [25]. These reactions have been exploited for a variety of applications such as templates for sensors, catalyst scaffolding, and insulation for interplanetary rovers [27–30]. Analysis of the products of these reactions have been studied by both solution and solid-state NMR detecting ^{27}Al and the ^{29}Si nuclei [26,31–34].

Therefore, during the membrane modification it is possible that a number of reactions may be occurring simultaneously. In particular, the sol–gel reaction may be occurring in a form of competitive reaction with the alumina surface as the proposed condensation mechanisms were very similar [25]. Initial investigations of ^{29}Si nuclei in solution state NMR (data not shown) didn't yield detectable chemical shift changes of the silane peak as would have been expected [26,31,35]. It was noted that in both the sol–gel reaction and in the attachment condensation reaction, methanol should be produced as a by-product. Furthermore, as methanol (MeOH) should have a distinct ^{1}H and ^{13}C NMR signal, it would be a much better target analyte for observation than the ^{29}Si shifts would be for monitoring both of these reactions. This process has already been observed under other reaction conditions for the purpose of determining hydrolysis kinetics [36].

Solution ^{1}H and ^{13}C NMR were used to examine the potential hydrolysis of the ODTMS methoxy groups under the current membrane modification conditions. A ^{1}H NMR spectrum of free ODTMS in chloroform-d (Fig. 2) was obtained and the methoxy protons

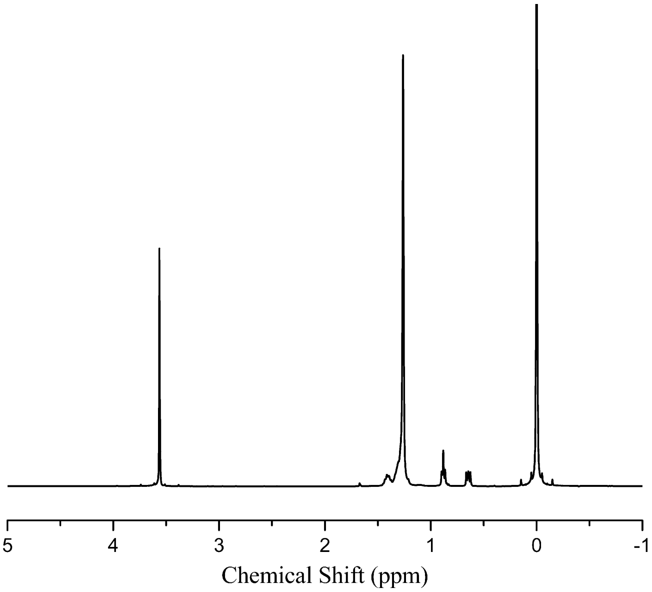

Fig. 2. Solution ^{1}H NMR spectrum of free ODTMS in chloroform-d. The peak at 3.52 ppm is assigned to the nine methoxy protons. The peak at ~1.4 ppm is assigned to the 32 backbone methylene protons. The peak at ~0.9 ppm is assigned to the three terminal methyl protons. The peak at ~0.6 ppm is assigned to the two methylene protons of the carbon directly bonded to the silicon atom.

(whose chemical shifts remained unchanged in different solvent conditions) assigned to the peak at 3.52 ppm.

To demonstrate that production of methanol could be used to monitor the hydrolysis, a spectrum of ODTMS in the reaction solution along with a methanol spike was obtained (Fig. 3). The chemical shift of the silane methoxy peak at 3.52 ppm is fully resolved from the MeOH peak at 3.33 ppm. Aliquots of reaction conditions with and without a membrane present were used for solution NMR.

The resulting spectrum from an aliquot with a membrane present is shown in Fig. 4. A small observable signal from methanol at 3.33 ppm is observed. Integration of the peaks corresponding to the ODTMS and methanol provides the relative% of methanol concentration to ODTMS of ~2%. Converting to moles of methanol produced gives 90–100 μmoles in the entire solution. As is shown below, even this small amount of methanol present suggests enough is produced during the modification procedure that the ODTMS could be fully covalently bound to the surface. ^{13}C solution NMR was attempted as a verification of methanol production; however, given the relatively fewer carbon nuclei present, the lower natural abundance of ^{13}C, and the lower sensitivity of ^{13}C, no signal was observed. Positive control reactions were performed in reaction conditions where the sol–gel hydrolysis reaction (Eqs. (3) and (4)) is known to rapidly occur [26]. The solid precipitate of ODTMS (a product of hydrolysis and condensation) was filtered and an aliquot of the filtrate examined by solution NMR (data not shown). A very strong peak was present, and its identity as methanol was confirmed by spiking the sample with methanol and obtaining a subsequent spectrum.

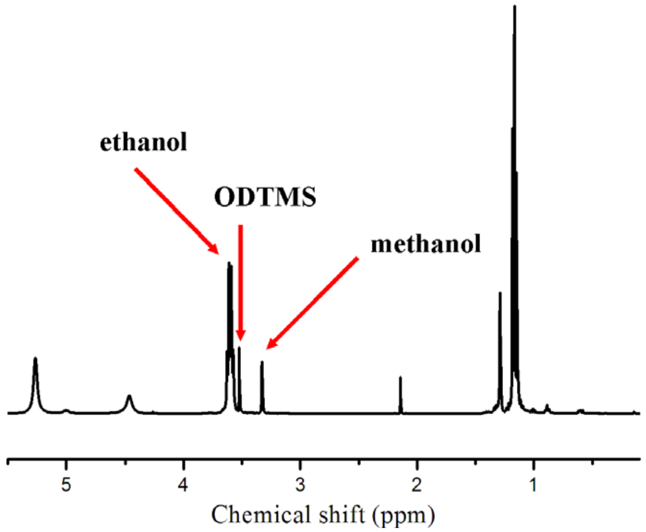

Fig. 3. Solution ^{1}H NMR spectrum of reaction mixture with a spike of methanol. The methanol at 3.33 ppm is fully resolved from (ODTMS, 3.52 ppm) and ethanol (3.61 ppm). Methanol is a potential product of the reactions that are occurring during silane attachment.

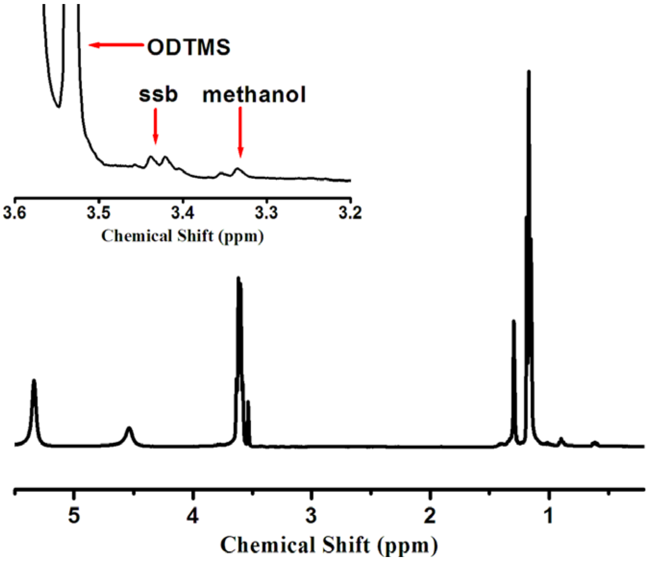

Fig. 4. Solution ^{1}H NMR spectrum of aliquot from reaction conditions (EtOH/buffer/ODTMS) with alumina membrane. Methanol production is indicated by the small peak at 3.33 ppm (inset). The quartet from 3.40 to 3.46 ppm is a spinning sideband (ssb) from ethanol due to imperfect non-spinning shims. The peak at 3.35 ppm is unknown.

3.3. Solid-state NMR analysis

The FT-IR results confirm the presence of the silane sidechains on the membrane, and the solution NMR results indicate that a small amount of methanol is produced, suggesting the possibility of covalent attachment to the membrane surface, but not unambiguously. Therefore, solid-state NMR (SSNMR), a powerful technique for characterizing non-crystalline, insoluble compounds, was used to more directly characterize the nature of the silane-surface interactions. ^{27}Al SSNMR was used to attempt to observe any changes in the alumina surface ^{27}Al chemical shifts due to the putative covalent attachment of the silane. The ^{27}Al SSNMR spectra (Fig. 5) show little difference between the blank and modified membranes, with the exception of a small change in the shoulder at ~5–10 ppm. These results are inconclusive, and this is not entirely surprising since it has been suggested there will only be a *ca.* 5 ppm shift in ^{27}Al chemical shifts due to Al–O–Si bond formation [32], and the experimental linewidth is much greater than 5 ppm due to structural heterogeneity of the membrane alumina nuclei.

Fig. 6 shows the ^{1}H SSNMR spectrum of a blank membrane overlaid by the ^{1}H SSNMR spectrum of the membrane modified with ODTMS. A large broad background signal is present in both

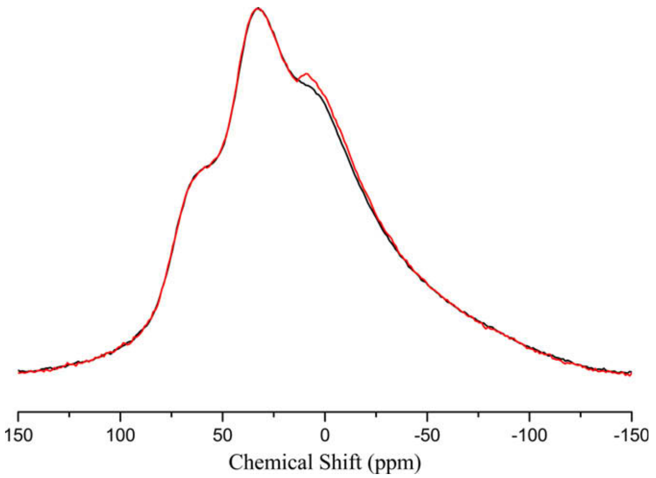

Fig. 5. Overlay of ^{27}Al SSNMR spectra for modified (red) and unmodified (black) membranes. There is only a modest difference in the shoulder at ~5–10 ppm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

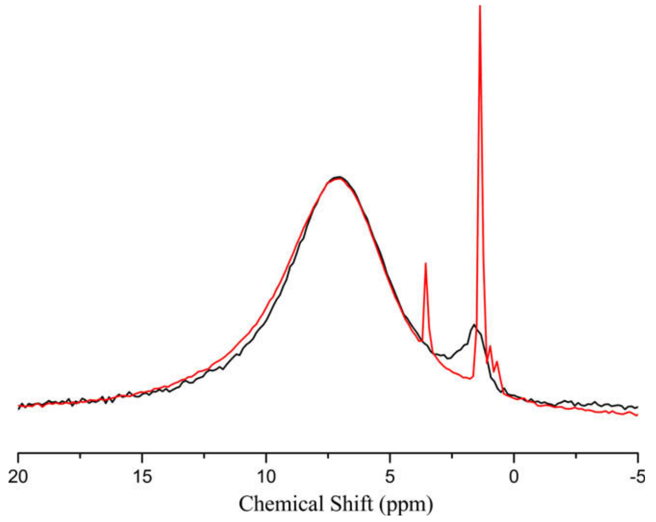

Fig. 6. Overlay of ^{1}H SSNMR spectra for modified (red) and unmodified (black) membranes. Peaks for the modified membrane occur in the region of both the methylene protons at ~1.4 ppm and the methoxy protons at ~3.6 ppm, which correlate well with the peaks of free ODTMS. An unknown contaminant shift occurs in the unmodified membrane at ~1.5 ppm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

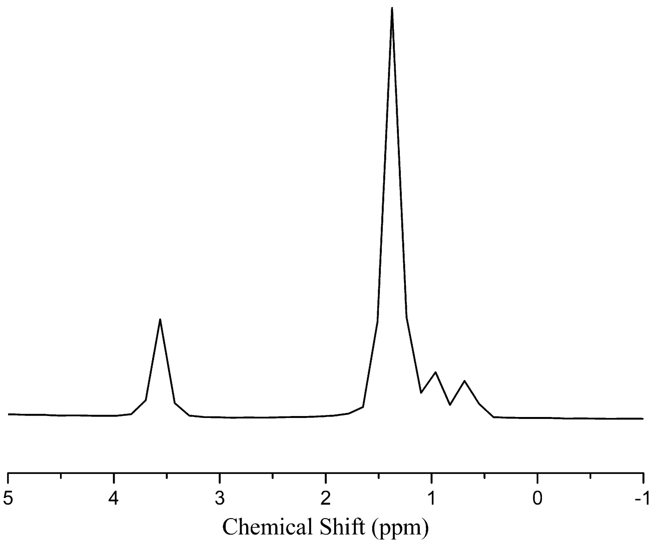

Fig. 7. ^{1}H SSNMR spectrum for a membrane modified with ODTMS. The broad background signals have been removed by repeated CPMG pulse sequences (see text) and the horizontal scale expanded to better view the ^{1}H signals. The peak patterns and integrated intensities (see text) indicate that most methoxy moieties remain intact on the surface of the membrane.

spectra, but the peaks from the ODTMS are clearly present at ~3.6 ppm and ~1.4 ppm in the spectrum of the modified membrane. The background signal can be removed by use of a CPMG pulse train, as discussed above. Fig. 2 shows a solution ^{1}H NMR spectrum of free ODTMS in chloroform-d for comparison to the SSNMR results of the membrane modified with ODTMS with background removed (Fig. 7). The specific methoxy and methylene peaks of the ODTMS can now be observed more easily and their quantitative integrated peak intensities can be measured. Integration of the SSNMR spectrum provides a ratio (methoxy protons: methylene and methyl protons) of approximately 1:4.62 ± 0.2. For comparison, the fully intact ideal ratio from ODTMS in solution would be 9:37 or 1:4.11 (Fig. 2).

As stated above, the amount of ODTMS bound to the membrane is 5.7 mg on a 150 mg membrane, or 15 μmoles per membrane. Using the information on pore characteristics (% porosity, pore size, membrane thickness and membrane diameter) provided by the manufacturer (www.whatman.com/PRODAnoporeInorganicMembranes.aspx), an estimation of ODTMS bound to the membrane provides approximately 14 molecules/nm^{2} surface coverage. For comparison, monolayer surface coverage for a C_{18} silane on Carbosil is 4 molecules/nm^{2} [37].

If all bound ODTMS molecules were losing all of their methoxy protons to hydrolysis or condensation for full covalent binding for every ODTMS attached to the surface, there would be no remaining methoxy protons present in the bound ODTMS. This scenario is not consistent with the SSNMR results in Fig. 7 which indicate that there are methoxy peaks present on the bound ODTMS. This result contrasts with previous published reports, in which complete covalent binding at full monolayer coverage to the alumina surface were proposed to be the mechanism of attachment for trichlorosilanes [9] and trimethoxysilanes [24]. However, these previous conclusions do not necessarily conflict with the current results, as dramatically different membrane modification procedures are used that may promote covalent binding and/or monolayer coverage.

Another possible model for binding is multilayer coverage with some amount of covalent binding of the ODTMS to the surface. The lowest layer has monolayer coverage where all ODTMS are either partially or fully covalently bound, and the remaining ODTMS molecules form a multilayer where the methoxy peaks remain intact and do not directly interact with the surface. Given the ratio of observed bound molecules to expected bound molecules of ~14:4 or 3.5:1, the ratio of methoxy protons: methylene and methyl protons can be predicted under different possible binding scenarios. For a fully covalently bound monolayer with a bi-layer of coverage above, the ratio of $O{-}CH_3{:}CH_2 + CH_3$ would be 18:111 or 1:6.17. This is sufficiently outside the error of the data as to be unlikely. However, if only a single methoxy peak from the monolayer hydrolyzes during attachment and the methoxy groups from the upper ODTMS layers remain completely intact, this provides an integrated proton ratio of 24:111 or 1:4.625, which agrees well with the ratio observed in the SSNMR experiment (i.e. 1:4.62). Therefore, a model for ODTMS binding under these reaction conditions that is consistent with the current data is as follows. ODTMS binds in approximately tri-layer coverage, where the lower monolayer has on average a single covalent Si–O–Al bond between the silane and the surface. The remaining methoxy groups of the monolayer ODTMS remain effectively intact.

Additionally, the relatively narrow linewidths of the bound ODTMS protons suggest that the motions of these molecules place them in the extreme narrowing motional regime. This result is satisfied if the molecules are indeed in the form of some multilayer, where significant molecule motion is expected to be present. Further work is being performed to investigate these hypotheses further.

4. Conclusions

Based on FT-IR, solution NMR and SSNMR data, it is proposed that the combination of the activity and increased pH of the buffer, as compared to the protocol by Fyfe et al. [26], contribute to inhibiting the sol–gel reaction and complete covalent surface condensation reactions. The data are consistent with a model where ODTMS forms a multilayer attachment to the surface of the membrane, with the lowest layer forming a single Si–O–Al covalent bond. The remaining methoxy groups on the lowest ODTMS layer are intact, as are all ODTMS methoxy groups in the upper layers. Enough methanol is produced during the modification and observed via solution ^{1}H NMR to provide full covalent attachment, but the SSNMR results from the bound ODTMS conflict with this result, and are consistent with this new model for attachment. These results are important in that they attempt to answer a long-standing question as to the nature of the silane attachment process. Additionally they suggest that attachment occurs in relatively simple and gentle conditions, which may facilitate future applications. Given their stability under repeated rinsings, and the significantly modified transport properties this work offers a potentially less demanding and greener protocol for modifying alumina nanoporous membranes as compared to other protocols [3,9,24].

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