



Probing the influence of water on silica surface modification during amine grafting for enhancing CO₂ adsorption

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ARTICLE INFO

Keywords:

Amine grafting
Wet grafting
Silanol density
Siloxane bridge
CO₂ capture
Adsorption
Decarbonisation

ABSTRACT

Amine-grafted adsorbents are promising materials for carbon capture, but their adsorption efficiency and hydrothermal stability still require improvement. This study examines how water addition influences silica surface modification during amine grafting with (3-aminopropyl)triethoxysilane (APTES). We used ²⁹Si cross-polarization magic-angle spinning (CPMAS) and direct-observation ²⁹Si NMR spectroscopy with proton decoupling to test the common assumption that water increases the surface silanol content of silica-based sorbents. Our findings indicate a different mechanism. BET analysis and NMR results show that water promotes the hydrolysis of APTES ethoxy groups. This accelerates condensation with surface silanol sites and enables a more complete reaction between APTES and the silica surface. A reduction in Q⁴ sites further supports this mechanism, suggesting that water induces structural rearrangement of surface siloxane bonds, generating additional reactive silanol groups for grafting. These mechanistic insights explain previously reported improvements observed in wet-grafted sorbents, including enhanced sorption kinetics, better thermal stability, improved regenerability, stronger CO₂ interaction, and increased selectivity. The enhanced performance is linked to the formation of more uniform siloxane bridges through hetero- and homo-condensation reactions of hydrolysed APTES molecules. Overall, this work highlights the central role of water in tuning the silica surface during amine grafting. By clarifying how water shapes the grafting mechanism, the study provides a pathway for designing more efficient and durable sorbents that can support scalable carbon-capture technologies and broader decarbonisation goals.

1. Introduction

Rising CO₂ levels from 280 ppm pre-industry to over 420 ppm in recent times are driving global warming and severe climate impacts [1–3]. To stay below 2 °C, nations are pursuing net-zero goals using strategies such as renewables and efficiency, with carbon capture and storage (CCS) playing a critical role in decarbonising power and industry [4–6] [5]. Amine scrubbing, traditionally used in CO₂ capture from flue gases using chemical absorption. While effective, the technology is associated with high energy demand for regeneration [7]. Solid adsorbents have been considered as an alternative solution that can potentially reduce the energy demand. A class of solid sorbents are amine-functionalised adsorbents (AFA) are a promising class of adsorbents that incorporate amine-modified solid supports, such as silica [8,9], alumina [10–12], metal-organic framework (MOF) [13,14], activated carbon [15] and aluminosilicates [16], to enhance CO₂ capture through chemisorption and physisorption mechanisms. This consideration as a

promising alternative is attributed to several factors, including lower energy requirement for regeneration, non-corrosiveness, and tuneable surface chemistry [17]. Silica-based amine sorbents are known to possess faster adsorption kinetics, stability, interaction strength and adsorbent selectivity during multicomponent adsorption when compared with their non-functionalised counterparts. These factors characterise optimal application of CO₂ capture technologies, and collectively influence the efficiency, cost-effectiveness, and, consequently, can enable the deployment of CO₂ capture technologies.

Studies carried out by Maresz et al. [18], Rim et al. [10], and Lin et al. [19] reveal that the efficacy of amine-functionalised adsorbents is significantly influenced by the surface chemistry of the support material. Hence, functionalization capabilities are heavily dependent on surface properties, which affect the distribution and reactivity of amine groups [20]. The stability of AFAs is crucial for their long-term viability and commercial relevance. This includes both chemical, cyclic, and thermal stability to ensure that the adsorbent maintains its performance over

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<https://doi.org/10.1016/j.cej.2025.171448>

Received 29 July 2025; Received in revised form 20 November 2025; Accepted 30 November 2025

Available online 2 December 2025

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multiple adsorption-desorption cycles without significant degradation [21]. The kinetics of adsorption and desorption are key to the efficiency of CO₂ capture processes. Faster adsorption kinetics reduce cycle time and increase throughput, while rapid desorption kinetics are essential for efficient regeneration of the adsorbent, and subsequently continuous operation [22]. The interaction strength between CO₂ and the adsorbent surface is crucial as it directly impacts the adsorption capacity and efficiency. This is due to the isosteric heat of adsorption which quantifies interaction strength provides insight into binding strength and the energy requirements for adsorbent regeneration [23,24].

Silica-based AFA can be synthesised primarily through impregnation or grafting. During impregnation, amine-based adsorbents are synthesised within a temperature range of 25 to 80 °C. During this process, amine molecules become physically attached to the support surface due to Van der Waals forces and hydrogen bonding between the amine and silica supports [25]. Impregnation is most effective when employing amino polymers with large chains, which generate substantial Van der Waals forces, facilitating the retention of amines in the pores and thereby enhancing cyclic retention than what would be obtained if polymers with short chain were used [26]. Grafting, also known as tethering, involves the covalent bonding of amines to organosilane on the target surface, resulting in multiple covalent bonds per amine centre within the adsorbent matrix. The formation of covalent bonding in the grafting then results in achieving greater cyclic and thermal stability [9,27,28].

It was shown that the addition of water during the grafting process can potentially increase amine loading, reduce synthesis time, and conserve energy by enabling synthesis at temperatures below 85 °C [29–33]. Anyanwu et al. [30] observed that the addition of water during synthesis led to higher capture capacities at elevated temperatures when utilising SBA-15 as a support structure. This phenomenon was attributed to the possible increase in silanol density which led to formation of tridentate attachment for aminosilane, thereby improving amine loading, cyclic and thermal stability of the adsorbent. While it is recognised that wet grafting enhances CO₂ capture, there remains a gap in understanding how the addition of controlled amount of water during grafting impacts the surface chemistry of the support material, and how a possible change in the surface chemistry can impact adsorption kinetics, stability, interaction strength and selectivity during multicomponent adsorption.

Accordingly, this study aims to investigate how the addition of water during grafting affects the surface chemistry of the support material. Accordingly, it examined how potential changes in surface chemistry influence adsorption kinetics, stability, interaction strength, and adsorbent selectivity during multicomponent adsorption. Solid-state nuclear magnetic resonance (NMR) was employed to acquire information on the local chemical environment of silicon atoms on the adsorbent surface. The synthesised AFA sample was characterized using Fourier transform infrared (FTIR), thermogravimetric analysis (TGA) and a sorption analyser. Results obtained showed a substantial effect of wet grafting on the rate of adsorption, interaction strength, CO₂ selectivity, and cyclic and thermal stability. By investigating the role of water during grafting and its impact on the surface chemistry of silica-based adsorbents, the research provides insights that can guide the development of more efficient adsorbents. The findings demonstrate that rather than increasing the silanol density as widely recognised, wet grafting enhances hetero- and homo-condensation reactions which tend to strain surface siloxane on silica material, leading to structural rearrangement of surface siloxane. This results in availability of more hetero-condensation reaction sites for hydrolysed amine groups, and a more complete reaction with the silica surface. This improved reaction leads to better adsorption kinetics, stronger interaction strength, increased CO₂ selectivity, and enhanced thermal and cyclic stability, making the adsorbents a possible candidate for long-term industrial use. Furthermore, the study's exploration of multicomponent adsorption highlights the potential for these materials to perform effectively in complex gas

mixtures, a critical consideration for real-world flue gas applications. These findings directly tackle critical challenges in carbon capture, including material performance and operational costs, by providing practical strategies for developing more effective materials. This, in turn, improves process efficiency and scalability which are both critical for accelerating the commercialisation of adsorption-based carbon capture technologies and strengthening global progress toward decarbonisation.

2. Materials and method

2.1. Materials

Silica gel beads (mesh size 250, and the pore diameter 6 nm), (3-aminopropyl)triethoxysilane (APTES) and toluene (ACS reagent, ≥99.5 %) were procured from Sigma-Aldrich. Methane, nitrogen, and carbon dioxide gases (99.99 % purity) were supplied by BOC (UK), and deionized water was supplied from a Millipore Elix® apparatus.

2.2. Sorbent formulation and synthesis

Dry and wet grafting approaches were employed to examine the influence of water on silica surface modification. The functionalisation of silica gel entailed a grafting procedure conducted under inert reflux conditions. Fig. 1 illustrates a schematic of the synthesis setup. Initially, 1 g of silica gel beads was subjected to degassing in a vacuum oven at 150 °C for 4 h. Subsequently, the flask and reflux apparatus were purged with nitrogen, and 40 ml of toluene was introduced into the flask. For the dry grafted samples, (3-aminopropyl)triethoxysilane (APTES) was added to the toluene solution, while for the wet grafted samples, 0.1 ml of deionized water was incorporated into the mixture of toluene and APTES. Following this, the degassed silica sample was introduced into the flask. The mixture was then heated to 85 °C and left under reflux while being stirred for 18 h. The grafted silica gel was recovered by filtration under vacuum suction and subsequently washed with ample toluene and methanol to remove unreacted amine [34]. Finally, the samples were dried in an oven at 50 °C for 6 h. 1.5 g, 2.5 g and 3.5 g of APTES were each used to synthesise dry and wet grafted samples used in this study. Given the hydrophilic nature of silica gel, the wet grafting route could potentially increase silanol density or introduce additional physisorbed water molecules that may condense with APTES during grafting. To verify whether wet grafting alone leads to an increase in silanol density or simply results in a hydrated silica surface, a control sample was synthesised via the wet grafting route without adding APTES. The samples were labelled as S-x-y, where 'x' denotes the type of grafting procedure employed (D for Dry, W for Wet), and 'y' represents the quantity in grams of APTES used in synthesising the sample (Table 1).

2.3. Material characterisation

2.3.1. Pore structure analysis

The specific surface area, pore volume, and pore size distribution of samples were measured through nitrogen physisorption measurements at −196 °C using a 3P Meso 222 sorption analyser. Prior to analysis, the samples underwent degassing under nitrogen (99.99 %) for 4 h at 120 °C. Specific surface areas were determined using the Brunauer–Emmett–Teller (BET) method within a relative pressure range of 0.05 to 0.20 [35]. The total pore volume (V_p) was calculated based on the amount of nitrogen adsorbed at a relative pressure (p/p₀) of 0.99 using the Barrett–Joyner–Halenda (BJH) method [36].

2.3.2. Solid-state NMR spectroscopy

All ²⁹Si magic angle spinning (MAS, $\nu_R = 12,000$ Hz, 303 K) solid state NMR were completed at 9.45 T ($\nu_0^{29}\text{Si} = 79.44$ MHz) using a Bruker Avance III HD spectrometer and a 4 mm double air bearing MAS probe.

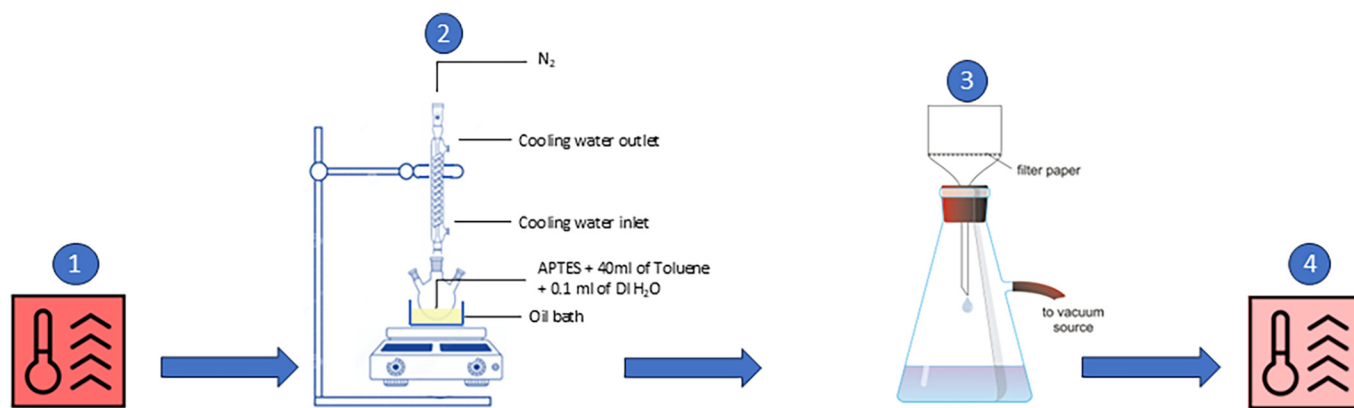


Fig. 1. Synthesis steps for dry and wet grafted samples. (1) vacuum heating of silica gel at 150 °C for 3 h; (2) reflux under N₂ blanket at 85 °C for 18 h; (3) vacuum filtration of sample with Methanol; and (4) drying of sample at 50 °C for 6 h.

Table 1

Sample formulation, surface characteristics, elemental analysis, and silane coverage and grafting efficiency of raw and functionalised silica gel. S_{BET} presents BET specific surface area; V_p presents pore volume; d_p presents pore size.

Sample	APTES mass (g)	S_{BET} (m ² /g)	V_p (cm ³ /g)	d_p (nm)	Elemental Analysis (%)				Grafted Silane (mg)	Amount of silane used for grafting (mol)	Amine coverage (group/nm ²)	Silane grafting efficiency
					mass (mg)	C	H	N				
Silica gel	–	426 ± 5	0.84	5.8	9.8	–	–	–	–	–	–	–
S_D_1.5	1.5	301 ± 3	0.55	4.9	9.6	6.6	2.2	2.4	0.0017	0.0068	2.43	25.41
S_W_1.5	1.5	173 ± 4	0.31	4.8	9.9	9.0	2.5	3.2	0.0023	0.0068	3.25	33.95
S_D_2.5	2.5	297 ± 2	0.52	4.9	10.7	4.8	1.8	2.8	0.0020	0.0113	2.86	17.90
S_W_2.5	2.5	140 ± 3	0.29	4.8	10.8	10.5	3.5	3.7	0.0027	0.0113	3.76	23.53
S_D_3.5	3.5	275 ± 3	0.45	4.8	11.6	9.5	2.8	3.3	0.0024	0.0158	3.38	15.14
S_W_3.5	3.5	91 ± 4	0.20	4.7	11.3	11.7	3.2	4.2	0.0030	0.0158	4.29	19.20

The experiments were referenced to solid kaolinite, at –91.7 ppm [37]. All spectra were recorded using a CPMAS sequence, with 100 kHz of proton ($\nu_{01H} = 399.89$ MHz) excitation and decoupling. A 70–100 % ramp was used with a 7.5 ms contact time and a 5 s recycle delay. For the direct observation ²⁹Si with proton decoupling, a 62.5 kHz excitation pulse was used with 100 kHz of proton decoupling. A measured 30-s recycle delay was utilised.

2.3.3. Fourier transform infrared (FTIR) spectroscopy

FTIR measurements were conducted using a Shimadzu Attenuated Total Reflection (ATR) spectrometer to verify the effective grafting of amine functional group, evaluate the progressive augmentation of functional moieties, and if due to the hydrophilic nature of silica gel if its surface gets wet or increases in silanol density during wet grafting in Toluene environment prior to addition of APTES. Few milligrams of powder sample were uniformly distributed onto the sample cell surface, and IR spectra were obtained within the range of 600 to 4000 cm^{–1} at a resolution of 4 cm^{–1}, with 50 scans per measurement in triplicates. Each spectrum was acquired by subtracting the background from the original spectrum. Baseline correction was done on the obtained spectra, and afterwards normalised.

2.3.4. Elemental analysis

The weight percentages of carbon (C), hydrogen (H) and nitrogen (N) grafted onto silica gel were determined using the Vario EL III Elemental, which employs the thermal combustion analysis method. In this analysis, 9–11 mg of each sample was utilised and repeated twice for each

test.

2.3.5. Adsorption rate, thermal and cyclic stability analysis

For the adsorption rate, thermal and cyclic analysis, a thermogravimetric analyser (TGA 8000, PerkinElmer) was employed. Adsorption rate was determined by carrying out a CO₂ capture test where 4–6 mg of sample was placed in the sample pan and heated under N₂ flow at 120 °C for 1 h to remove adsorbed volatiles. The sample was then cooled to 28 °C and exposed to CO₂ at a flow rate of 40 ml/min. Cyclic stability studies, involving 50 adsorption/desorption cycles, were conducted using 4–6 mg of the sample at 28 °C for the adsorption and 120 °C for the desorption, for each test.

The rate of CO₂ adsorption for the functionalised samples was determined from the differential thermogravimetric (DTG) curve. To ensure uniform heating during the determination of amine loading and thermal stability, 4–6 mg of the sample was placed in the sample pan and exposed to nitrogen at a flow rate of 60 ml/min. The temperature was ramped at a rate of 20 °C/min from 30 °C to 120 °C, held for 60 min, and then increased to 800 °C at the same heating rate. At 800 °C, the gas was switched to air and held for an additional 10 min to eliminate any residual carbonaceous material.

2.3.6. Adsorption isotherm measurements

Volumetric adsorption measurements for CO₂, CH₄, and N₂ equilibrium data were conducted using the 3P Meso 222 sorption analyser. Each sample (0.25–0.30 g) underwent degassing at 120 °C for 2 h, and the sample tube was immersed in a liquid bath (3P Instruments)

maintained at temperatures of 28 or 40 °C. The fixed dosing sorption method was employed to ensure uniform gas dosing of 3.1 ml/g for CO₂, 12.5 ml/g CH₄ and 1.6 ml/g for N₂ at all pressures. To fit the CO₂ gas adsorption isotherms, the dual-site Langmuir isotherm model [38], was used, Eq. (1).

$$n = m \left[\frac{\alpha k_1 P}{1 + k_1 P} + \frac{(1 - \alpha) k_2 P}{1 + k_2 P} \right] \quad (1)$$

where n is the absolute adsorption quantity under equilibrium temperature, T (K) and pressure, P (kPa), m is the maximum adsorption capacity (mol/g), α is the fraction of the second type of site ($0 < \alpha < 1$), K_1 and K_2 are the temperature-dependent equilibrium constant at sites 1 and 2, which can be expressed as $K_{1,2} = A_0 \cdot \exp\left(-\frac{E_0}{RT}\right)$, E_0 is the energy of adsorption (kJ/mol), A_0 is the pre-exponential coefficient and R is the ideal gas content where both E_0 and A_0 are independent of temperature (J/mol.K).

Because the CH₄ and N₂ adsorption profile demonstrates linearity in accordance with Henry's law [39], the Henry's model, Eq. (2), was used to fit the CH₄ isotherm.

$$q = KP \quad (2)$$

The isosteric enthalpy of adsorption was calculated using the measured isotherms at 28 °C and 40 °C and based on the Clausius Clapeyron Eq. (3), [40,41].

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{Ads}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3)$$

where H_{Ads} , is the isosteric enthalpy of adsorption, T_1 and T_2 are the isotherm temperatures of the relative pressures of P_1 and P_2 , and R is the universal gas constant.

2.3.7. Selectivity analysis

The separation factor ($\hat{S}$) [49] was used to determined selectivity using Eq. (4). As shown in Eq. (4), the separation factor is ratio that compares the adsorption capacities of two gases on an adsorbent. It gives the ratio of the amount of CO₂ adsorbed to the amount of another gas N₂ or CH₄ adsorbed under the same conditions. This method provides a quick assessment of an adsorbent's preference for CO₂ over another gas [27].

$$\hat{S} = \frac{q_i}{P_i} \times \frac{P_j}{q_j} \quad (4)$$

where q (mmol/g) and P (kPa) are equilibrium adsorption capacity and partial pressure of the gas species, respectively.

3. Results and discussion

3.1. Confirmation of functional group and effectiveness of wet grafting

Fig. 2 presents the FTIR spectroscopy analysis results for samples. These analyses also allowed for a comparison among the silica gel, dry-grafted, and wet-grafted samples to assess the impact of wet grafting. The peak at 1580 cm⁻¹ corresponds to the N—H bending (scissoring) vibration of primary amines, typically found in the 1650 cm⁻¹ to 1580 cm⁻¹ region of the spectrum [42] as can also be seen in the APTES spectrum, indicating the presence of amine groups. Additionally, the peak at 682 cm⁻¹ is characteristic of the N—H wagging vibration of primary amines, showing a medium-to-strong broad absorption in the region between 909 cm⁻¹ and 666 cm⁻¹ in the IR spectrum. The identification of N—H scissoring and wagging vibrations in the IR spectrum of the amine-functionalised adsorbents (AFA), which are absent in the spectrum of silica gel, confirms the successful synthesis of the AFA. Moreover, the peak intensities at 1580 cm⁻¹ and 682 cm⁻¹ are significantly higher in the wet grafted samples compared to the dry grafted samples. This difference is attributed to the increased concentration of APTES in the wet grafted samples.

Table 1 tabulates the elemental analysis was performed to determine the composition of a synthesised organic compound. The experimental values for C, H, and N recorded for all synthesised samples, which are absent in the silica gel sample, confirm the success of the synthesis process. Furthermore, the observed increase in nitrogen content with increasing APTES mass and between the dry and wet grafted samples further validates the effectiveness of the two different synthesis routes employed in this study.

3.2. Effect of wet grafting on pore structure

Nitrogen adsorption–desorption isotherms and pore size distribution of the samples at −196 °C are presented in Fig. 3a and b. All samples

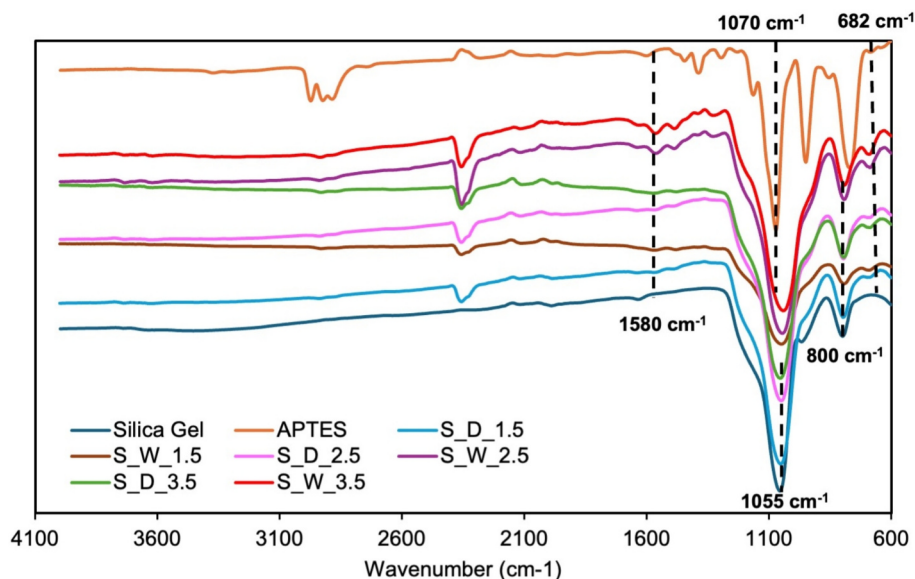


Fig. 2. FTIR spectrum for silica gel and amine functionalised adsorbent. 1055 cm⁻¹ presents Si-O-Si stretching vibration; 1580 cm⁻¹ represents N—H scissoring vibration; 1070 cm⁻¹ presents Si-O-C stretching vibration; 800 cm⁻¹ present Si-O-Si stretching vibration; and 682 cm⁻¹ presents N—H wagging vibration.

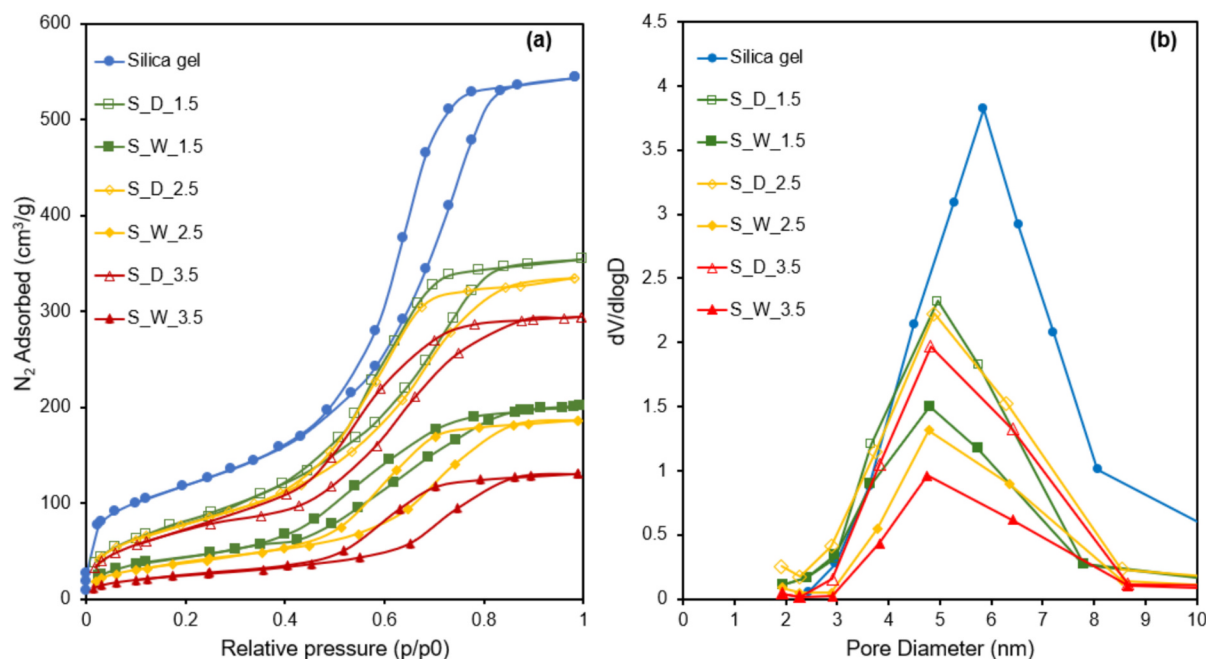


Fig. 3. Nitrogen adsorption-desorption isotherms at -196°C (a); Corresponding pore size distribution (b).

exhibited a type IV isotherm with an H2-type hysteresis loop, typical of silica gel materials. This behaviour can be attributed to pore-blocking/percolation in a narrow range of pore necks or to cavitation-induced evaporation with a larger size distribution of neck widths [43]. The introduction of APTES resulted in a reduction in both pore volume and specific surface area of the adsorbent as the quantity of APTES increased. Fig. 3a also shows that the grafting of APTES did not alter the pore structure of silica gel, as indicated by the maintenance of the H2-type hysteresis loop in all grafted samples. Consistent with previous studies, the wet grafted samples exhibited higher amine loading compared to their dry grafted counterparts, and amine loading increased with increasing APTES concentration among the wet samples. The change in pore size distribution for both dry and wet grafted samples was calculated from the N_2 isotherms up to $P/P_0 = 0.85$, marking the final saturation plateau, and is presented in Fig. 3b. Fig. 3b suggests the possibility of a homogeneous distribution of silane molecules within the pores of the silica gel. The narrow range of pore sizes, within ± 0.2 nm

grafted samples are above the theoretical value of 2.1–2.7 group/nm² reported by Sindorf and Maciel [48]. This can be ascribed to increased homo-condensation reaction in wet grafted samples as reported in the work done by Millot et al., [49]. These reactions cause a greater proportion of hydrolysed amine groups to become predominantly physisorbed onto the surface, with only limited anchoring to the silica framework through silanol groups. Consequently, a significant reduction in specific surface area (S_{BET}) and pore volume (V_p) is observed.

Similarly, the grafting efficiency, calculated using Eq. (6), was also influenced by the addition of water during the grafting process, as demonstrated in Table 1. The results indicate that wet grafted samples exhibited higher grafting efficiencies compared to their dry grafted counterparts. Additionally, for all the amine functionalised samples, the grafting efficiency was observed to decrease with an increase in the quantity of APTES used in the grafting process. This decline in efficiency is attributed to the increased presence of unreacted amines in the grafting solution as the amine concentration rises.

$$\text{Silane grafting efficiency } (\eta) = \frac{\text{Amount of silane grafted (moles)}}{\text{Amount of silane used for grafting (moles)}} \times 100 \quad (6)$$

for the amine-functionalised samples, indicates a uniform distribution of APTES [44–46]. The consistent pore sizes also suggest that the functionalization process has uniformly affected the samples, leading to a uniform modification of the pore structures.

The silane coverage, which estimates the silane density on the silica surface, was determined using Eq. (5) [47].

$$\text{Amine Coverage (group/nm}^2\text{)} = \frac{\text{Silane grafted} \times N_A}{\text{Surface area (m}^2\text{/g)} \times 10^{18}} \quad (5)$$

The addition of water during grafting resulted in an increase in silane coverage is presented in Table 1. As anticipated, increasing the concentration of APTES resulted in higher silane coverage, as more amine groups became available for hetero-condensation reactions with surface silanol groups. Furthermore, it is seen that the amine coverage of wet

^{29}Si CPMAS NMR spectra were recorded of silica gel, dry grafted and wet grafted samples to analyse the structural and functional characteristics of silicon environments. These systems contain both Q and T environments, where Q sites represent silicon atoms within the silicate framework, and T sites correspond to silicon atoms bonded to APTES.

The CPMAS NMR spectra, given in Fig. 4a, indicate that the wet grafted sample has an elevated peak in the trifunctional silicon structure (T^3) region, suggesting a higher level of functionalization compared to the dry grafted sample. In the T^3 environment (~ -68 ppm), each silicon atom in APTES forms Si–O–Si bonds with three adjacent silicon atoms, achieving complete cross-linking. This implies that wet grafting enhances the formation of a more comprehensive siloxane network,

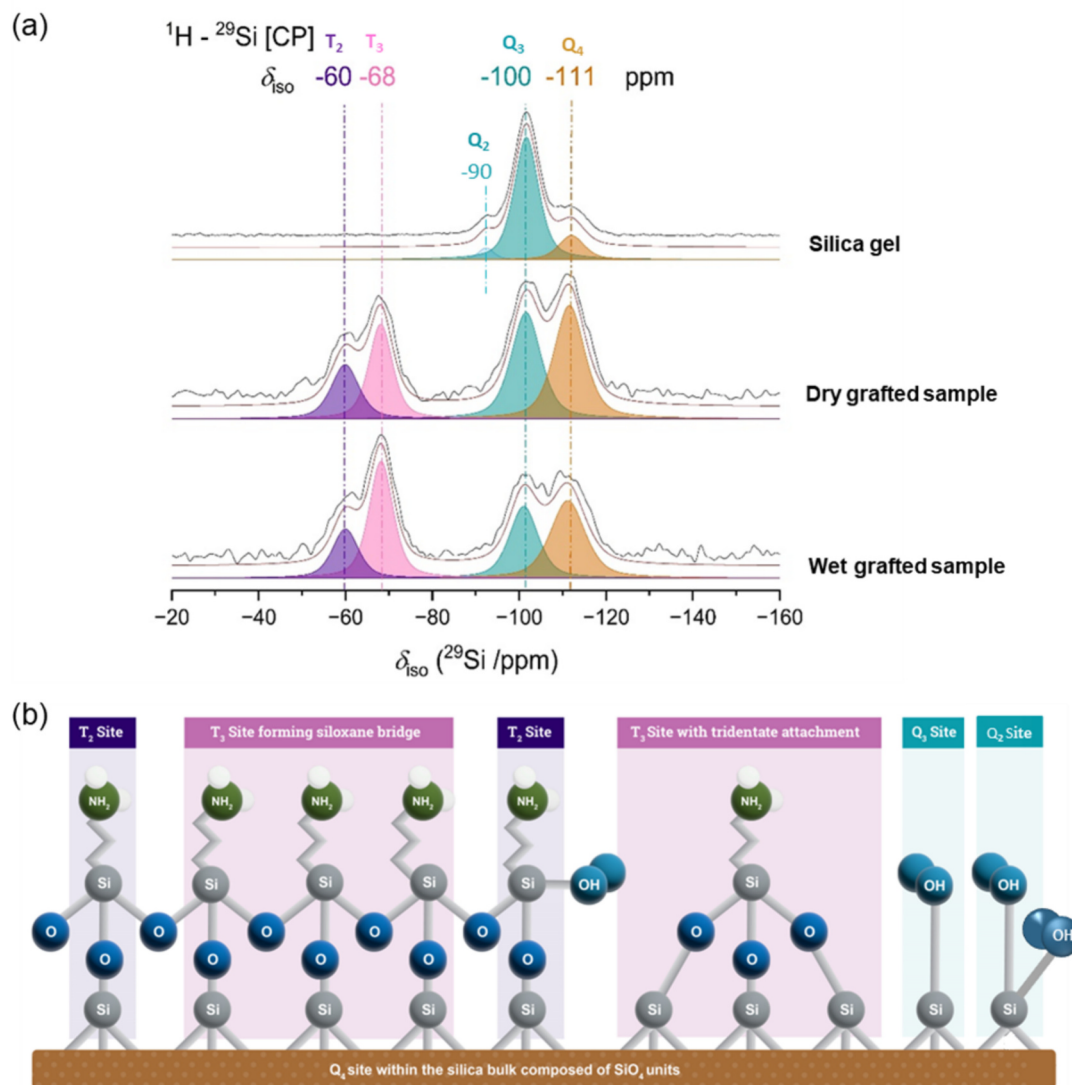


Fig. 4. ^{29}Si NMR CPMAS spectrum of dry and grafted AFA samples (a); Schematic conformation of T and Q sites in dry and wet grafted AFA samples (b).

facilitating stronger attachment of functional groups to the silica surface. The T^2 site, typically observed at ~ -60 ppm, indicates that the silicon atom in APTES is bonded to two other silicon atoms through Si–O–Si bonds, with the third oxygen either being part of a hydroxyl group (Si–OH) or acting as a terminal point in the network. Consequently, the T^2 silicon site, as shown in Fig. 4a, is partially cross-linked, lacking the full connectivity with three silicon atoms that is seen in the T^3 environment, as shown in Fig. 4b. Additionally, the NMR spectrum reveal a higher T^2 peak in the wet grafted sample compared to the dry grafted sample. This suggests that, since T^2 represents Si–O–Si bonds in a terminal network, the increase in the T^2 peak may indicate a greater extent of siloxane bridge formation, covering a larger surface area of the silica gel in the wet grafted sample. The BET results support this observation.

In the Q environment, Q^3 species (resonating at ~ -100 ppm) represent silicon atoms with three Si–O–Si bonds and one free hydroxyl group (Si–OH) on the silica network surface. Interaction with APTES leads to condensation reactions that consume Q^2 sites (~ -90 ppm) reduce Q^3 sites and generate T environments, as visualized in Fig. 4b. The lower Q^3 peak in the wet grafted sample indicates that the Si–OH groups on the silica surface reacted more extensively with APTES, leading to increased T^3 and T^2 peaks. This observation challenges the conventional belief that water in the grafting process increases the

density of silanol groups (Q^3) on the silica surface. Instead, the BET result and CPMAS NMR spectra suggest that water enhances APTES diffusion and promotes the hydrolysis of ethoxy groups, enabling a more complete reaction with the silica surface. The Q^4 environment (~ -111 ppm), representing fully condensed silicon atoms bonded to four other silicon atoms (SiO_4 units), shows the lowest peak in silica gel. This observation is largely because, as shown in the CPMAS NMR, signal intensity depends on the proximity of ^{29}Si nuclei to nearby ^1H atoms, as cross-polarization transfers magnetization from ^1H to ^{29}Si . In unmodified silica, Q^4 units typically located deeper in the bulk have limited proximity to protons, resulting in weaker CP efficiency. However, in functionalised silica, the presence of proton-rich species such as amines, hydroxyls, or adsorbed water near the surface enhances CP efficiency, even for Q^4 sites. Consequently, when comparing signals of silica gel and functionalised samples, the observed increase in Q^4 signal intensity in functionalised samples reflects improved polarization transfer rather than a true increase in Q^4 unit abundance. However, when comparing signals between proton rich species of dry and wet APTES functionalised samples, a lower peak in the wet grafted sample, indicates a reduction in silica surface atoms. This may result from APTES hydrolysis during wet grafting, where ethoxy groups undergo nucleophilic attack by water, producing silanol groups (–SiOH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) as by-products, [49] Eq. (7).

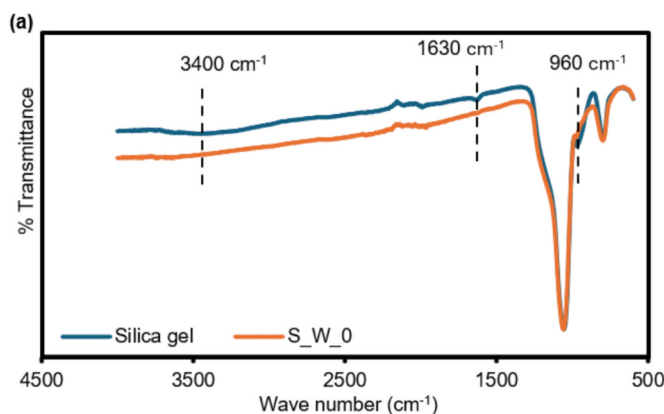
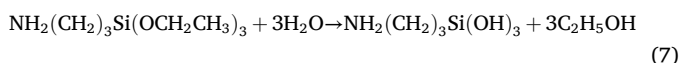


Fig. 5. FTIR spectrum for silica gel and control sample. 3400 cm^{-1} is assigned to hydrogen-bonded silanol groups; 1630 cm^{-1} represents bending vibration of adsorbed water molecules that are physically bound to the silica surface; 960 cm^{-1} represents stretching vibration of isolated surface silanol (a); ^{29}Si NMR CPMAS spectrum of control and silica gel samples.



The resulting silanol groups can react with silica atoms on the surface to form T^3 or T^2 sites, further depleting silicon atoms in the silica network at the surface of the silica gel.

In order to validate the observation from ^{29}Si NMR CPMAS result on silanol content and possible structural change to silica surface siloxane (Si-O-Si) due to wet grafting, FTIR, ^{29}Si NMR CPMAS and a direct observation ^{29}Si with proton decoupling NMR was carried out on the control sample (S_W_0). The FTIR spectrum of sample synthesised following the wet grafting protocol using only 0.1 ml of DI and 40 ml Toluene is shown in Fig. 5. This was necessary to ascertain the possibility of silica surface wetness or increase in silanol content which could react with APTES during grafting.

The spectrum of sample S_W_0 in Fig. 5 shows several key changes on its material's surface compared to the pure silica gel. The most noticeable change is the significant reduction in the intensity of the peaks at $\sim 3400\text{ cm}^{-1}$ and $\sim 960\text{ cm}^{-1}$. This indicates that the toluene has displaced the adsorbed water molecules and/or interacted with the surface silanol groups, forming a heterogeneous azeotropic mixture which boils at approximately $84.1\text{ }^\circ\text{C}$ [50]. The displacement of physisorbed water molecules on the surface of silica gel by toluene explains the decrease in the $\sim 1630\text{ cm}^{-1}$ peak intensity as well. CPMAS NMR spectra in Fig. 5b confirm this observation as there is no noticeable increase in the Q^3 and Q^2 peaks. Thus, although silica gel is hydrophilic, wet grafting at $85\text{ }^\circ\text{C}$ in toluene does not increase silanol density, as the toluene–water azeotrope (bp $84.1\text{ }^\circ\text{C}$) removes physisorbed water during the process.

The direct observation ^{29}Si with proton decoupling NMR test was carried out to confirm if there are possible structural changes to the surface siloxane of silica gel during wet grafting as suggested by the CPMAS NMR. In CPMAS, magnetization is transferred from abundant ^1H spins to low- γ nuclei such as ^{13}C , and ^{29}Si to enhance sensitivity, but the resulting intensities are not strictly quantitative due to relaxation and cross-polarization dynamics [51,52]. In contrast, direct observation ^{29}Si with proton decoupling uses direct excitation of the observed nucleus with proton decoupling only during acquisition, providing quantitative spectra when sufficiently long recycle delays are used [53].

The direct observation ^{29}Si with proton decoupling NMR result reveal as seen in Fig. 6 that wet grafting of APTES molecules on silica gel can cause structural rearrangement or strain on the silica network near the surface. A study by Talavera-Pech et al. [54] supports this observation, as they reported a loss of mesopore structure in MSNs functionalized with 15 % APTES. In our work, we attribute this behaviour to changes in structural coordination, whereby the reduction of the Q^4 signal indicates a transition from Q^4 environments to less-coordinated Q^3 or Q^2 environments. This transition creates additional hetero-

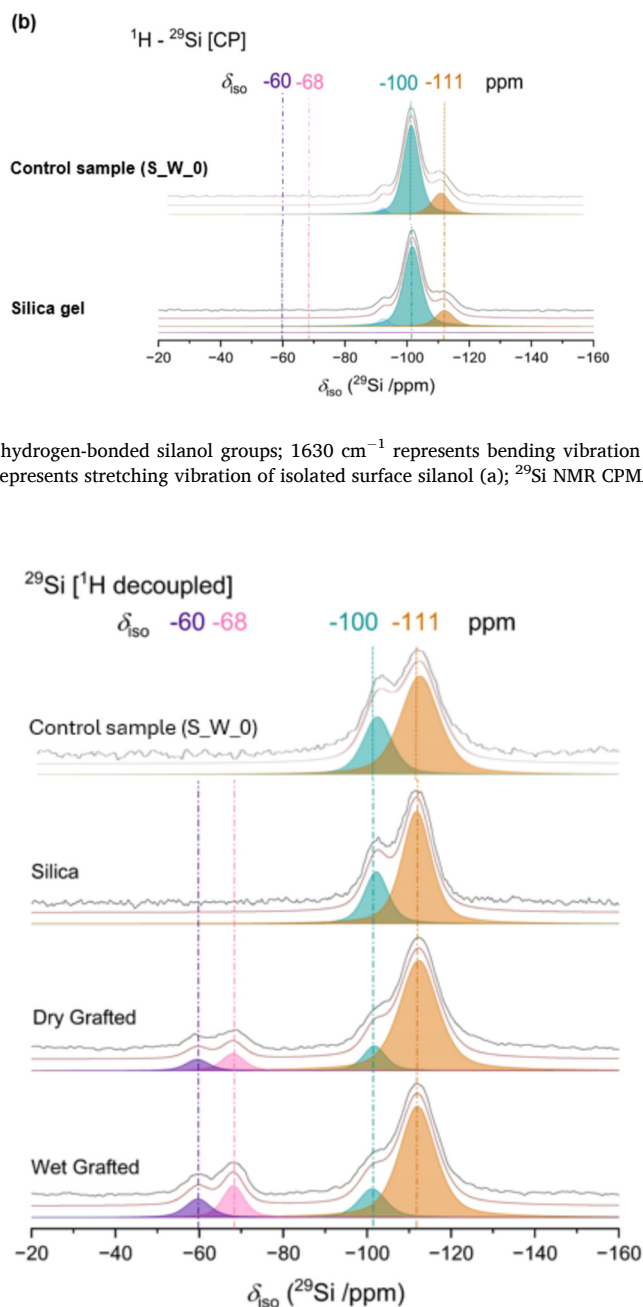


Fig. 6. Direct observation ^{29}Si with proton decoupling NMR spectrum with peak integration result.

condensation sites, thereby increasing the T^3 environment peak observed in the wet-grafted samples. From both FTIR and solid-state NMR analyses, we conclude that controlled water addition during grafting does not hydrate silica but instead promotes aminosilane hydrolysis and subsequent condensation. This induces structural rearrangements of near-surface siloxanes, creating additional condensation sites and thereby enhancing amine loading in wet-grafted samples. An

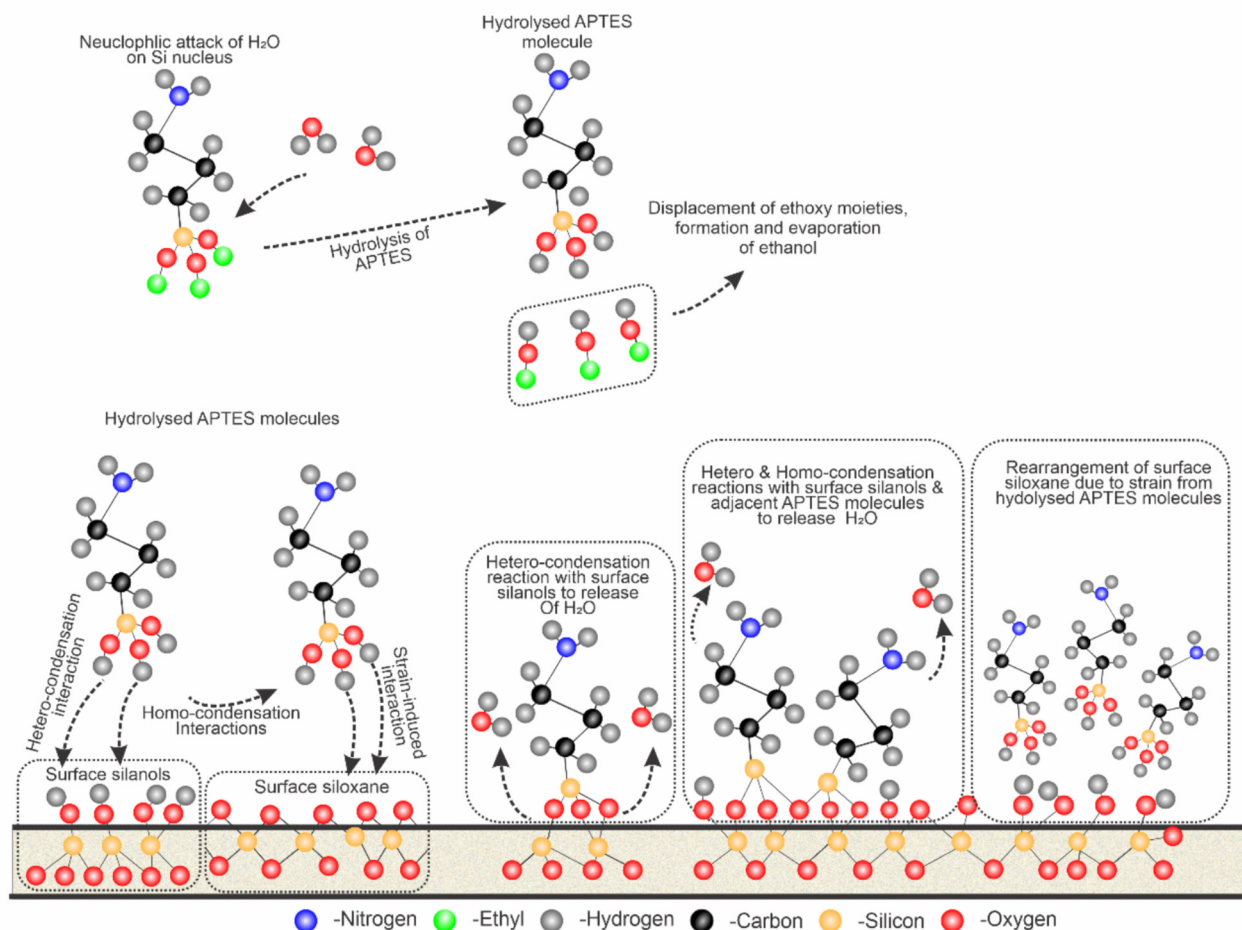


Fig. 7. Illustration of proposed wet grafting mechanism based on FTIR and solid-state MMR results

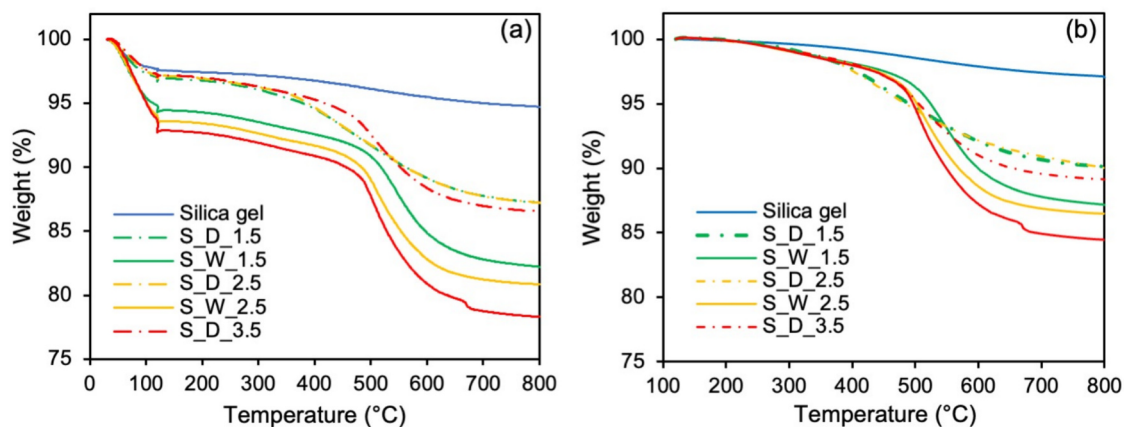


Fig. 8. TGA percent weight change for silica gel and both wet and dry grafted samples from 30 °C to 800 °C (a); TGA percent weight change for wet and dry grafted samples from 120 °C to 800 °C (b).

illustration of the proposed mechanism is shown in Fig. 7.

The thermal stability of the samples was evaluated using thermogravimetric analysis to determine the effect of water addition during the grafting process. The TGA curves as shown in Fig. 8a indicate that all wet-grafted samples exhibited greater initial weight losses when heated from room temperature to 120 °C compared to the dry-grafted samples, with increasing amine loading. Specifically, the S_W_3.5 sample recorded a 7.2 % loss, S_W_2.5 showed a 6.5 % loss, and S_W_1.5

demonstrated a 5.58 % loss. In contrast, the dry-grafted counterparts exhibited lower weight losses, with S_D_3.5 showing a 2.8 % loss, S_D_2.5 a 3.0 % loss, and S_D_1.5 a 3.2 % loss. This initial weight loss region is attributed to the desorption of physically adsorbed water molecules, solvents, and gases, which are weakly bonded to the surface of the adsorbent and thus desorb easily when heated to 120 °C. These findings indicate that the wet-grafted samples contained more physisorbed water molecules than the dry-grafted samples, as expected.

Fig. 8a illustrates that the wet-grafted samples exhibited higher amine loading and physisorbed water molecules than the dry-grafted samples, with amine loading increasing proportionally to the APTES concentration. Specifically, the wet-grafted samples showed amine loadings of 9.18 mmol/g for S_W_1.5, 9.65 mmol/g for S_W_2.5, and the highest loading of 11.11 mmol/g for S_W_3.5. In comparison, the dry-grafted samples recorded amine loadings of 7.07 mmol/g for S_D_1.5, 7.19 mmol/g for S_D_2.5, and 7.77 mmol/g for S_D_3.5. Further analysis of the TGA profiles, as depicted in Fig. 4b, within the temperature range of 120 °C to 800 °C, confirms that all wet-grafted samples had higher amine loadings compared to their dry-grafted counterparts.

From Fig. 8b, it is evident that both S_D_1.5 and S_W_1.5 samples experienced a mass loss of 1.2 % as heating continued from 120 °C to 330 °C. This mass loss corresponds to the region where the loss of surface hydroxyl groups occurs due to the condensation reaction of adjacent silanol groups, as well as the volatilization of unreacted silane coupling agents or byproducts from the functionalization process. At 380 °C, the decomposition of amine molecules began for the dry grafted sample (S_D_1.5), and complete degradation was observed at 800 °C. Conversely, the amine molecules in the wet grafted sample exhibited thermal stability up to 480 °C, with an additional weight loss of 1.7 % between 330 °C and 480 °C, attributed to the volatilization of unreacted ethoxy groups in APTES. The increase in thermal stability by 100 °C for the wet grafted sample is attributed to the larger coverage of Si – O – Si bridges, which link a grafted amine molecule to other grafted amino-silane, thereby enhancing the thermal stability of the sorbent, as illustrated in Fig. 4b. A similar observation is noted for S_D_2.5 and S_W_2.5 where amine degradation occurs at approximately 370 °C for the dry grafted sample and approximately 470 °C for the wet grafted sample. However, this trend was not found in the S_D_3.5 and S_W_3.5 samples as the amine in both samples became thermally unstable at 475 °C and hence leached from the silica substrate as seen in Fig. 8b. A possible explanation for this observation would be that the concentration of APTES in S_D_3.5 is sufficient to form the needed coverage of Si – O – Si bridge that enhances thermal stability of the amine adsorbent.

3.3. Effect of wet grafting on CO₂ adsorption, adsorption rate and enthalpy of adsorption

Fig. 9 illustrates that amine-functionalised adsorbents exhibit a significantly higher CO₂ capture capacity compared to non-functionalised adsorbents. The silica gel sample captured 0.33 mmol/g of CO₂, whereas the functionalised samples demonstrated markedly higher capture capacities: 0.81 mmol/g for S_D_1.5, 0.98 mmol/g for S_D_2.5, 1.17 mmol/g for S_D_3.5, 1.12 mmol/g for S_W_1.5, 1.37 mmol/g for S_W_2.5, and 1.25 mmol/g for S_W_3.5. Furthermore, the data indicates that wet-grafted samples generally possess a higher capture capacity than their dry-grafted counterparts, consistent with existing literature. This finding suggests that wet-grafted adsorbents are more suitable for capturing CO₂ from diluted or ultra-low CO₂ streams, as at least 40 % of the capture, characterized by chemisorption, was achieved in this region.

As anticipated, an increase in the concentration of APTES resulted in

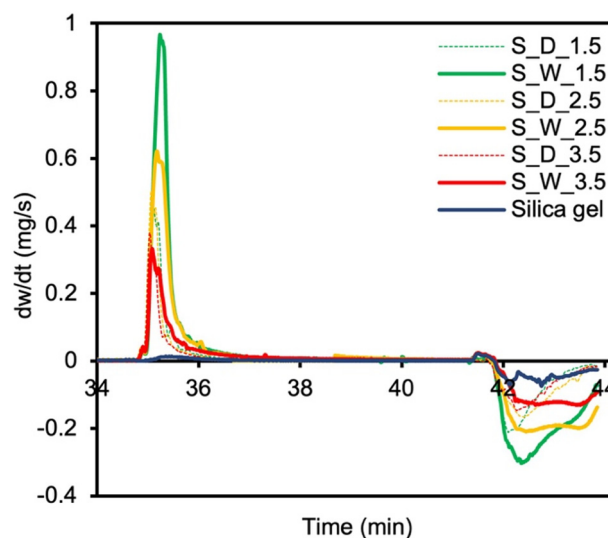


Fig. 10. DTG curves of amine functionalised silica gel at 28 °C.

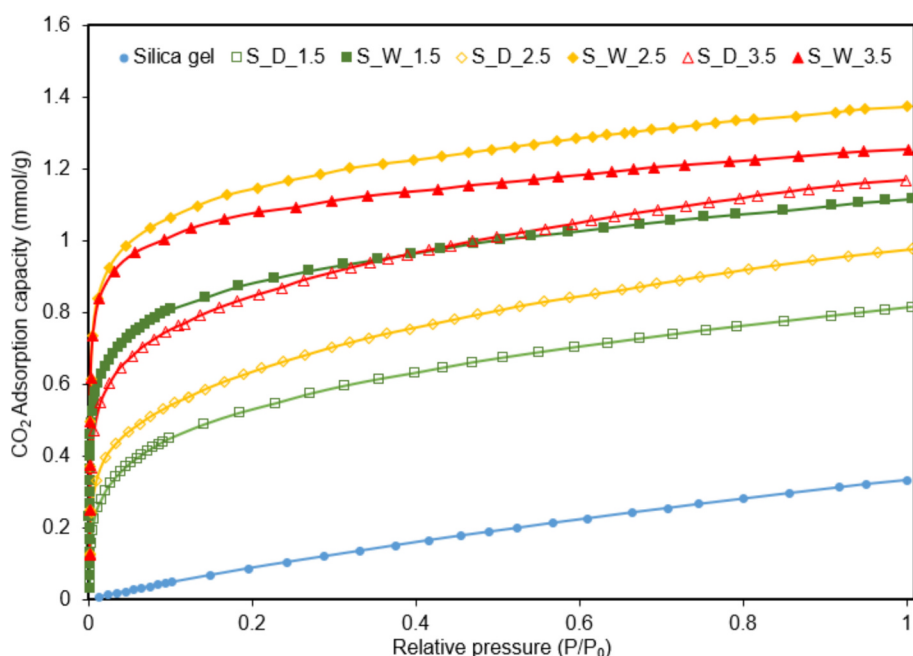


Fig. 9. CO₂ adsorption isotherms of raw and functionalised silica gel at 28 °C. Solid lines represent model fit.

an increased capture capacity for dry-grafted samples, attributable to the increased silane coverage on the silica surface. However, this trend did not hold for wet-grafted samples; S_W_2.5 exhibited the highest capture capacity, rather than S_W_3.5. The capture capacity of S_W_3.5 was observed to be 8.61 % lower than that of S_W_2.5, despite having a silane coverage 15.2 % higher. This discrepancy is likely because of pore filling with amine groups. As the grafted APTES increased from 2.5 g to 3.5 g, the pore volume reduced by 31.02 %. In contrast, the increase in APTES from 1.5 g to 2.5 g resulted in only a 6.45 % reduction in pore volume. This suggests that excessive amine loading due to higher APTES concentrations leads to the physical filling of the pores with amine groups, thereby reducing the total pore volume available for CO₂ adsorption. Consequently, there is less physical space for CO₂ molecules to be adsorbed, directly impacting the capture capacity.

The DTG curve presented in Fig. 10 offers detailed insights into the kinetics of CO₂ capture by the amine adsorbents utilised in this study, as well as the effects of varying grafting conditions on adsorption behaviour. This information is crucial for both fundamental research and practical applications in CO₂ capture technologies.

It is observed that, except for samples functionalised with 3.5 g of APTES, wet samples functionalised with 1.5 g and 2.5 g of APTES exhibit superior adsorption rates compared to their dry grafted counterparts. Specifically, S_W_1.5, which achieved the fastest adsorption rate of 0.96 mg/s, adsorbed CO₂ at a rate twice that of S_D_1.5, which had an adsorption rate of 0.45 mg/s. Similarly, S_W_2.5 recorded a CO₂ adsorption rate of 0.61 mg/s, while S_D_2.5 had a lower rate of 0.48 mg/s. The enhanced adsorption rate observed with water-aided grafting is attributed to the more uniform silane coverage achieved on the silica gel surface, which minimizes silane clustering at pore entrances and thereby improves access to CO₂ adsorption sites within the adsorbent pores. Consequently, under water-aided grafting, lower amine concentrations minimize silane clustering and steric hindrance, thereby improving CO₂ accessibility to adsorption sites and enabling more CO₂ capture per unit time.

However, among the wet grafted samples, as the APTES loading increases, the adsorption rate is observed to decrease. A possible explanation for this phenomenon, is the increase in silane layer due to formation of Si-O-Si bonds resulting from self-condensation reaction between APTES molecules hydrolysed by the addition of water during grafting. This creates a surface barrier that limits the diffusion of CO₂ into active sites within the pore wall [55]. This also potentially explains the observed trend reversal for samples functionalised with 3.5 g of APTES,

where thermal stability data suggests the formation of extensive silane layering in comparison to other samples.

The isosteric enthalpy of adsorption (ΔH_{ads}) characterizes the binding energy between the adsorbate and adsorbent. It is anticipated that this value varies with the uptake during the adsorption process. At zero to low coverage, the magnitude of the isosteric enthalpy of adsorption predominantly reflects the binding strength of the material's strongest binding sites [41]. Fig. 11 indicates that S_W_2.5 possesses stronger binding sites, with a ΔH_{ads} value of 105 kJ/mol compared to 95 kJ/mol for S_D_2.5, and 32.40 kJ/mol for silica gel. These few high-energy sites in S_W_2.5, however, become rapidly saturated at low uptake levels. Following the occupation of these preferred binding sites, the enthalpy of adsorption typically decreases with increasing uptake. The stepwise ΔH_{ads} pattern seen in S_W_2.5 sample suggests engagement with chemically distinct environments. At low coverage, CO₂ likely forms strongly bound ammonium carbamate pairs with isolated primary amines, accounting for the high initial enthalpy [10,56]. As loading increases, interactions shift to more hindered or polymerized regions, where cooperative effects such as carbamate-carbamic acid pairing briefly elevate the adsorption energy before it declines toward weaker sites like bicarbonate-forming or physisorptive regions [57,58]. As pore filling progresses, ΔH_{ads} eventually approaches the interaction energy of CO₂, equivalent to the enthalpy of liquefaction or evaporation, which is 17 kJ/mol for CO₂. For S_D_2.5, ΔH_{ads} remains significantly higher than the 17 kJ/mol threshold because the adsorption isotherms have not reached the pore-filling regime at the highest measured pressure of 100 kPa. This suggests that S_D_2.5 would likely continue to adsorb CO₂ at higher pressures, as it has not yet achieved pore filling, and its interaction energy exceeds the CO₂ enthalpy of liquefaction or evaporation. A material such as S_W_2.5, with an enthalpy of adsorption of 105 kJ/mol, is more thermodynamically favourable for CO₂ capture than conventional monoethanolamine (MEA) solvents. This enthalpy translates to an estimated regeneration energy of approximately 2.39 GJ per tonne of CO₂, which is substantially lower than the typical steam demand of about 3.7 GJ per tonne of CO₂ in standard MEA-based systems [59].

3.4. Effect of wet grafting on material selectivity and cyclic stability

The CO₂/N₂ and CO₂/CH₄ selectivity profiles at 28 °C and 40 °C provide important insights into the behaviour of primary amine-functionalized silica sorbents prepared via dry and wet grafting routes. These results are particularly relevant to applications such as direct air capture (DAC) and biogas upgrading, where gas compositions and operating temperatures vary considerably. From Fig. 12, we see that at 28 °C which represent conditions closely resembling ambient air, the wet-grafted sorbent demonstrates markedly higher selectivity for CO₂ over both N₂ and CH₄, especially at low CO₂ partial pressures ($P/P_0 < 0.04$). This high selectivity is critical for DAC, where CO₂ concentrations are very low (~400 ppm). The improved performance of S_W_2.5 at these low pressures is likely due to the more uniform dispersion and accessibility of amine groups resulting from the presence of water during grafting. This structural advantage promotes stronger chemisorption of CO₂ via carbamate formation while reducing non-specific uptake of N₂ and CH₄. In contrast, S_D_2.5 shows lower selectivity, which could stem from more densely packed, less accessible aminosilane domains formed during the dry grafting process. Raising the temperature to 40 °C which is typical of biogas upgrading conditions further enhances the CO₂ selectivity of S_W_2.5. This improvement is attributed to thermally activated CO₂-amine interactions and increased gas diffusivity, which together boost adsorption efficiency in CO₂-rich environments such as biogas (CO₂ ~40–60 %). Interestingly, S_D_2.5 exhibits a more complex response to temperature. While its CO₂/N₂ selectivity decreases at 40 °C, possibly due to the desorption of weakly bound CO₂ or destabilization of surface complexes, its CO₂/CH₄ selectivity increases. This suggests that the temperature rise may suppress CH₄ physisorption more effectively than it hinders CO₂ chemisorption, thereby sharpening the selectivity

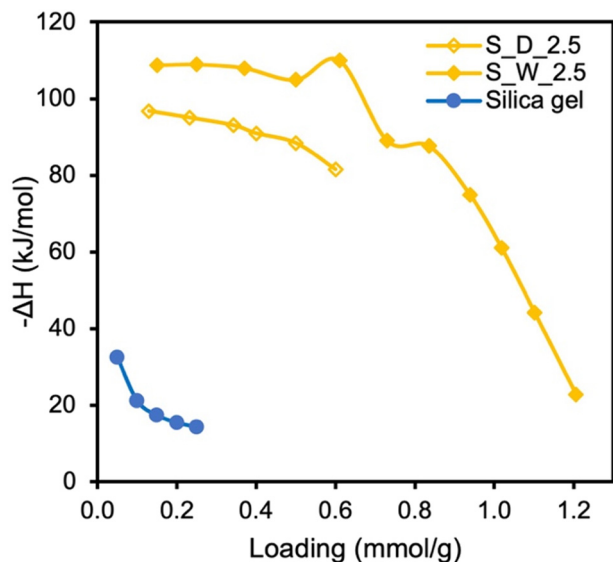


Fig. 11. Isosteric enthalpy of adsorption of CO₂ for Silica gel, S_D_2.5 and S_W_2.5 derived from 28 °C and 40 °C.

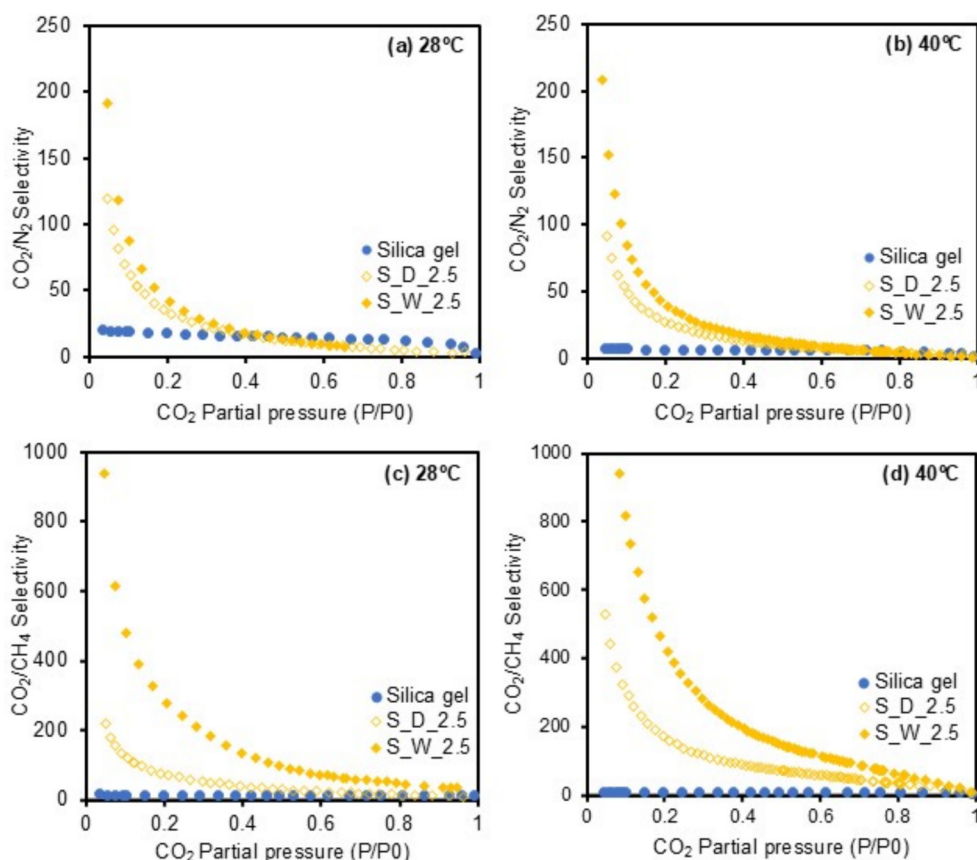


Fig. 12. CO₂/N₂ selectivity of Silica gel, S_D_2.5 and S_W_2.5 at 28 °C (a); CO₂/N₂ selectivity of Silica gel, S_D_2.5 and S_W_2.5 at 40 °C (b); CO₂/CH₄ selectivity of Silica gel, S_D_2.5 and S_W_2.5 at 28 °C (c); CO₂/CH₄ selectivity of Silica gel, S_D_2.5 and S_W_2.5 at 40 °C (d).

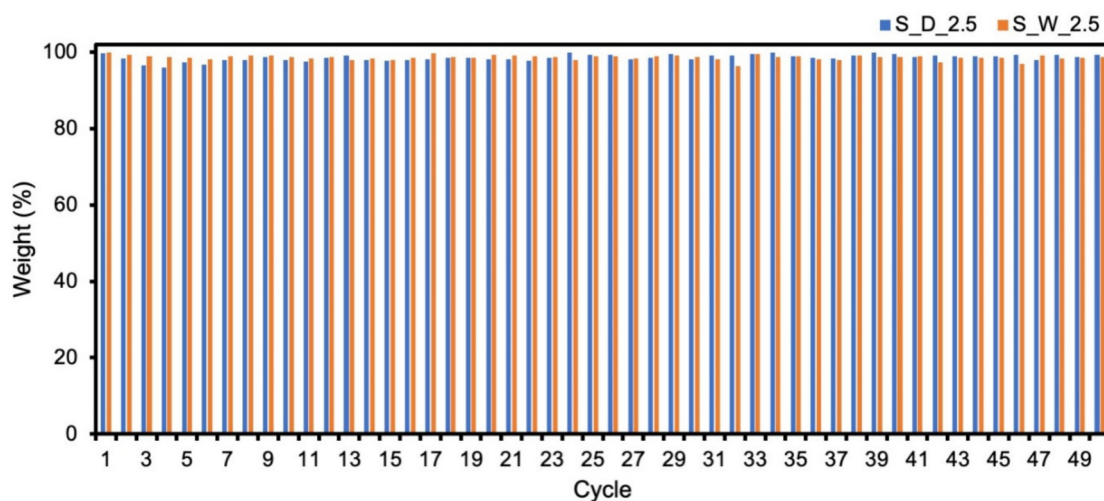


Fig. 13. Cyclic stability of S_D_2.5 and S_W_2.5 operating at 28 °C for adsorption and 120 °C for desorption cycle.

contrast. Overall, temperature plays a dual role in shaping sorbent performance. It enhances CO₂ chemisorption kinetics especially in wet grafted amine sorbents where amine sites are exposed and reactive while also suppressing physisorption, which disproportionately affects N₂ and CH₄ uptake. These effects combine to yield higher selectivity, particularly in the CO₂/CH₄ system. S_W_2.5 benefits consistently from thermal activation, while S_D_2.5 shows a mixed response due to less favourable site accessibility and internal diffusion limitations. In summary, water-aided grafted sorbents emerges as the more effective sorbent for both

DAC and biogas applications due to its high, thermally stable CO₂ selectivity. The differences observed between the sorbents highlight the critical role of amine distribution and surface accessibility features that are strongly influenced by the grafting method in determining the performance of CO₂-selective materials.

The cyclic stability measurements (Fig. 13) reveals that both samples endured 50 cycles without any noticeable loss in weight after the first cycle as all variations in weight were within a range of ± 1 %. This indicates that the grafting method used in material synthesis was effective.

The presence of the Si-O-Si bridge in both samples was sufficient to prevent the leaching of the grafted amine during temperature swings between 28 °C and 120 °C.

4. Conclusion

This study investigated the role of water in enhancing key properties of adsorbents, including adsorption capacity, heat of adsorption, selectivity, kinetics, thermal stability, and regenerability. ²⁹Si CPMAS and direct observation ²⁹Si with proton decoupling NMR spectroscopy was employed to analyse the surface chemistry of wet and dry grafted samples, providing insights into how these surface modifications influence adsorbent performance. The results revealed that wet grafting promotes the formation of a cross-linked siloxane network, evidenced by higher T³ peaks (fully cross-linked silicon environments) and partially cross-linked T² peaks. This indicates stronger functional group attachment and improved surface coverage compared to dry grafting.

Contrary to the widely accepted notion that water during grafting increases surface silanol density on the silica surface, the findings from both FTIR and solid-state NMR analyses show that water does not increase surface silanol content. Instead, water hydrolyses the aminosilane, which subsequently condenses with both the native silica silanols and adjacent aminosilane molecules. The increased extent of hydrolysed aminosilanes imposes strain on near-surface siloxane networks, driving structural rearrangements and transitions from coordinated siloxane to silanol environments. These transitions create additional sites for hetero-condensation, ultimately enabling higher amine loading in the wet-grafted samples.

These insights help explain the key improvements observed in wet-grafted samples, including a 21–53 % increase in adsorption rate (depending on amine loading), up to 100 °C higher thermal stability, ±1 % weight variation after the first cycle, enhanced CO₂ uptake, ~35 % lower regeneration energy than MEA scrubbing, and improved CO₂/N₂ and CO₂/CH₄ selectivity at 28 °C and 40 °C. These enhancements are attributed to the formation of more uniform siloxane bridges in wet-grafted samples, driven by the hydrolysis and condensation reactions of APTES in the presence of water. The findings underscore the critical role of water in optimizing the grafting process by promoting APTES hydrolysis and diffusion. This knowledge is vital for improving adsorbents used in direct air capture (DAC) applications, ensuring their scalability and reliability. Optimized adsorbents will enhance DAC's contribution as part of a broader portfolio of negative emissions technologies (NETs), which are essential for offsetting residual emissions and achieving the Paris Agreement targets. Following the promising outcomes of this study, it is essential to evaluate the performance of the wet-grafted AFA samples under conditions involving humidity as well as the presence of SO_x and NO_x gases. This will enable a deeper understanding of their stability and suitability for real-world CO₂ capture applications.

CRedit authorship contribution statement

Briggs M.O. Ogunedo: Writing – review & editing, Writing – original draft, Validation, Software, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Gregory Rees:** Writing – review & editing, Methodology, Formal analysis, Data curation. **Seyed Ali Nabavi:** Writing – review & editing, Supervision, Funding acquisition, Formal analysis.

Declaration of competing interest

The authors confirm that there are no known financial or personal conflicts of interest that could have influenced the research presented in this paper.

Acknowledgement

Briggs Martins Onyinyechukwu Ogunedo expresses gratitude to the Petroleum Technology Development Fund (PTDF), Nigeria, for the doctoral study scholarship (Award Number: PTDF/ED/OSS/PHD/BOO/1710/20) and to Imo State University, Owerri, Nigeria, for their support.

Data availability

The data supporting this article is domiciled in the Cranfield university repository and can be accessed using this link <https://doi.org/10.57996/cran.ceres-2768>

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2026-01-01

Elsevier

<https://doi.org/10.1016/j.cej.2025.171448>

Ogunedo BMO, Rees G, Nabavi SA. (2026) Probing the influence of water on silica surface modification during amine grafting for enhancing CO₂ adsorption. Chemical Engineering Journal, Volume 527, January 2026, Article number 171448