Konversi 15(1) (2026) 36-44

KONVERSI
Homepage:
https://ppjp.ulm.ac.id/journal/index.php/konversi

Process intensification of silica amination through ultrasound-assisted impregnation: Toward highly efficient amino-functionalized particles

Hendrix Abdul Ajiz[1,*], Widiyastuti Widiyastuti[2], Heru Setyawan[2], Ade Sonya Suryandari[3], Nove Kartika Erliyanti[1]

[1]*Department of Chemical Engineering, Faculty of Engineering and Science, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya 60294, Indonesia*
[2]*Department of Chemical Engineering, Faculty of Industrial Technology and System Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo Surabaya 60111, Indonesia*
[3]*Department of Chemical Engineering, Politeknik Negeri Malang, Malang 65141, Indonesia*

ARTICLE INFO

Article history:

Received: 09 February 2026
Received in revised form: 21 April 2026
Accepted: 21 April 2026

Keywords:

Alkoxysilane ligands, macroporous silica, surface morphology, acoustic cavitation, material processing

ABSTRACT

Amine-functionalized porous silica is a highly promising material for sustainable carbon capture; however, increasing amine loading is often limited by pore blocking and diffusion resistance of the modifying agents. This study proposes an ultrasound-assisted ex-situ impregnation strategy to enhance aminopropyl grafting efficiency within macroporous silica matrices. Macroporous silica particles were synthesized via a sol-gel spray drying route using an anionic surfactant template and subsequently functionalized with alkoxy-aminopropyl ligands. The results demonstrate that the synergistic effects of ultrasonic irradiation and macroporous morphology significantly improve ligand distribution homogeneity, suppress particle agglomeration, and promote aminopropyl penetration into the internal pore network while minimizing pore blocking induced by self-condensation. FTIR and TG-DTA analyses confirm a substantial increase in aminopropyl loading up to 0.9610 mmol g^{-1} silica, nearly twice that achieved by conventional impregnation, despite a reduction in specific surface area due to pore filling. Overall, this approach provides an efficient and scalable pathway for producing amine-rich silica adsorbents with enhanced accessibility and strong potential for sustainable CO_2 capture applications.

1. Introduction

Silica is one of the most widely utilized porous inorganic materials across a broad range of strategic applications, including gas adsorption, heterogeneous catalysis, separation processes, chemical sensing, and as a support material in biomedical and energy-related systems [1,2,3]. The widespread adoption of silica is primarily attributed to its structural tunability, which enables the engineering of high specific surface areas through controlled synthesis routes, particularly via the incorporation of templating strategies in the formation of hybrid or mesostructured particles [4,5,6,7]. In contrast, non-structured silica particles synthesized without deliberate pore-forming techniques typically exhibit relatively low specific surface areas, often accounting for only a small fraction approximately 10% of those achieved by other inert porous materials such as activated carbon [3,8,9]. Despite this limitation, silica offers several intrinsic advantages that make it preferable for applications under demanding operating conditions. Notably, silica exhibits superior thermal and chemical stability compared to carbon-based materials, which, although characterized by exceptionally high surface areas, are generally more susceptible to structural degradation and chemical instability under harsh environments. This robustness allows silica-based materials to maintain structural integrity and performance in extreme conditions, thereby broadening their applicability in industrial and technological systems. Beyond its favorable physicochemical stability, silica is particularly attractive due to the relative ease of surface functionalization. The presence of surface silanol groups (Si-OH) enables the grafting of various functional moieties through both physical interactions, such as van der Waals forces, and chemical bonding mechanisms involving condensation reactions [10,11,12,13]. Among the various surface modification strategies, amine functionalization has attracted considerable attention owing to its pivotal role in enhancing chemical affinity between the silica surface and target species, including carbon dioxide, heavy metal ions, and reactive molecules in catalytic systems [14,15,16]. However, despite its significant potential, the fabrication of amine-modified porous silica particles remains constrained by several process-related challenges. Limitations such as inefficient mass transfer during grafting, non-uniform distribution of amine groups, and restricted

* Corresponding author.
Email: hendrix_abdul.tk@upnjatim.ac.id
http://dx.doi.org/10.20527/k.v15i1.25507

This open access article is distributed under a Creative Commons Attribution (CC-BY-SA) 4.0 license

accessibility of functionalization agents to internal pore structures often result in suboptimal amine loading and low grafting efficiency. These constraints directly affect the functional performance of the resulting materials and underscore the need for advanced process strategies capable of overcoming the inherent limitations of conventional amination approaches [10,14,17,18].

Conventionally, silica amination is primarily carried out via impregnation or grafting methods using organosilane compounds such as g-aminopropyltriethoxysilane (APTES) or other amine-containing ligands. During the amination process, which proceeds through hydrolysis and subsequent condensation reactions, interactions between the silica particle surface and the modifying agent solution enable the attachment of amine ligands through both physical adsorption and chemical bonding [10,15,19]. These interactions facilitate the formation of siloxane linkages between the surface silanol groups (Si-OH) of the silica matrix and the organosilane molecules. Despite the widespread adoption of this approach in surface engineering of silica particles, several inherent limitations remain. Conventional amination routes often suffer from prolonged reaction times, non-uniform spatial distribution of amine functionalities, and relatively low precursor utilization efficiency. The limited amine loading is partially attributed to the stoichiometric requirement between surface hydroxyl groups and amine ligands that can be accommodated within the silica matrix. Theoretically, the formation of a fully condensed tridentate aminopropyl configuration requires the involvement of three surface hydroxyl groups to anchor a single aminopropyl ligand [18,20,21]. However, under practical synthesis conditions, incomplete condensation frequently occurs, leading to the formation of bidentate or monodentate binding configurations. These partially anchored species are inherently less stable, resulting in weakly bound amine functionalities on the silica surface [14]. In addition to bonding limitations, mass transfer constraints present a major challenge in the amination of porous silica. The diffusion of amine-containing modifying agents into the amorphous pore network of silica particles particularly in micro- to mesoporous structures is often severely hindered. This diffusion resistance is primarily associated with pressure gradients between the internal pore environment and the external particle surface, which restrict the effective penetration of amination agents into the pore interiors. As a consequence, the amination process tends to be localized predominantly on the external surface of the particles rather than within the internal pore structure. This phenomenon is particularly detrimental, considering that the majority of the available surface area in porous silica matrices resides within the pore network rather than on the external particle surface [10].

Within the framework of modern process engineering, the concept of process intensification has emerged as an innovative strategy to enhance chemical reaction efficiency and mass transfer performance through the modification of operating conditions or the application of non-conventional energy fields. Among the various intensification techniques, the use of ultrasonic irradiation has gained increasing attention due to its ability to induce acoustic cavitation phenomena [22,23]. During ultrasound-assisted impregnation, cavitation events generate localized microjets, shock waves, and intense microturbulence, which collectively promote accelerated mass transfer, enhanced reactant penetration into porous structures, and improved reaction homogeneity at the microscale. The application of ultrasonic energy effectively mitigates diffusion limitations encountered during the injection of modifying agents into the pore network of silica particles, particularly in systems characterized by elevated internal pore pressures. By disrupting stagnant boundary layers and inducing dynamic fluid motion within the pore channels, ultrasonic irradiation facilitates the transport of amination agents toward the internal surface of porous silica matrices. Although ultrasonic techniques have demonstrated significant effectiveness in accelerating reaction kinetics and improving product quality across various material synthesis processes, their systematic implementation in silica amination remains relatively underexplored [24,25]. The integration of conventional impregnation with ultrasonic assistance thus represents a promising process intensification strategy to overcome the intrinsic limitations of traditional silica amination routes. Through ultrasound-assisted impregnation, the interaction between silica surfaces and amination agents can be substantially strengthened, enabling more uniform and efficient formation of amine functionalities within a reduced processing time. Furthermore, ultrasonic irradiation can disrupt particle agglomeration induced by partial condensation reactions, which often lead to interparticle bridging and clustering of modified silica matrices. This deagglomeration effect contributes to the formation of more homogeneous particle structures with higher amine loading capacities [10,14,26]. Collectively, this intensified approach not only enhances the functional performance of the synthesized materials but also offers notable advantages in terms of energy efficiency and process sustainability factors that are increasingly critical in the development of next-generation functional materials.

Therefore, this study aims to comprehensively investigate the intensification of silica amination through ultrasound-assisted impregnation for the production of highly efficient amine-functionalized silica particles. The work focuses on evaluating the influence of ultrasonic irradiation on surface characteristics and amine functionalization efficiency, as assessed by the quantity of amine loading successfully anchored within the porous silica matrix. An ex-situ synthesis route was employed, in which porous silica particles were first prepared as inert solid matrices prior to surface modification. Porous silica was synthesized via a sol-gel method using sodium silicate (Na_2SiO_3) as the silica source, followed by an ion-exchange process to obtain a salt-free, stable colloidal silica precursor. An anionic surfactant, sodium lauryl sulfate (SLS), was introduced as a self-assembly template to engineer the porous structure. The removal of the templating agent was carried out simultaneously

with particle formation through a spray-drying process, resulting in porous silica particles with tailored internal structures. Subsequently, the as-prepared porous silica particles were subjected to amination via impregnation both in the absence and presence of ultrasonic irradiation to systematically assess the effect of ultrasound on amine loading efficiency. All modification processes were conducted under ambient temperature and pressure conditions. The experimental outcomes were then employed as the basis for elucidating the mechanistic role of ultrasonic irradiation in enhancing mass transfer, surface accessibility, and overall functionalization efficiency during silica amination. A dual-mechanistic approach is introduced to mitigate diffusion barriers of amine functionalities in porous silica, leveraging the synergistic effects of engineered macroporosity and ultrasonic cavitation. The cavitation-induced microjets and shockwaves promote enhanced mass transfer, facilitating deeper and more uniform incorporation of aminopropyl groups within the silica pore architecture. The findings of this study are expected to provide both fundamental insights and practical implications for the development of more efficient, controllable, and sustainable synthesis routes for amine-functionalized silica materials.

2. Materials and Methods

2.1. Materials

All chemicals employed in this study were of analytical or reagent grade and were used as received without further purification. Sodium silicate (Na_2SiO_3), with a silica content of 27% and a SiO_2:Na_2O molar ratio of 3.3, was obtained from Merck and used as the primary silica precursor. A cation-exchange resin (Flotrol-007) and hydrochloric acid (HCl, 37%, analytical reagent grade) were supplied by Mallinckrodt and utilized for the ion-exchange treatment during precursor preparation. Potassium hydroxide (KOH, analytical reagent grade) was purchased from Merck and employed for pH adjustment. Porous structure engineering was facilitated by the use of an anionic surfactant, sodium lauryl sulfate (SLS, technical grade), supplied by CV. Citra Sari Kimia Indonesia. For surface functionalization, g-aminopropyltriethoxysilane (APTS, 99%, analytical reagent grade) was procured from Sigma-Aldrich and used as the amination agent. Absolute ethanol (C_2H_5OH, reagent grade), obtained from Merck, served as the solvent during the modification process. Demineralized water with a pH of 5, supplied by UD. SIP Indonesia, was used throughout all synthesis and surface modification procedures.

2.2. Ex-situ route aminopropyl-modified silica particles synthesis

The ex-situ amination strategy employed in this work was deliberately designed as a two-step process, comprising the controlled formation of porous silica particles followed by post-synthetic surface functionalization. This approach enabled precise decoupling between pore structure engineering and surface chemistry modification, thereby providing a robust platform for evaluating the effect of ultrasound-assisted impregnation in subsequent stages. Initially, sodium silicate (Na_2SiO_3) was dissolved in demineralized water at 60°C to achieve a silica concentration of 0.7 M. The resulting solution was subjected to a batch cation-exchange process to replace Na^+ ions with H^+ ions, yielding an active silicic acid species ($Si(OH)_4$). Ion exchange was conducted under magnetic stirring for 30 min until a homogeneous solution with a pH of approximately 2 was obtained. This step was critical for eliminating residual alkali ions and ensuring a highly reactive silica precursor for subsequent condensation. The formation of silica nanoparticles was then initiated via the controlled, dropwise addition of 0.1 M KOH solution, which acted as a condensation catalyst. The reaction was allowed to proceed until the system reached a pH of 10, resulting in a stable silica nanofluid. To engineer the internal pore architecture, an anionic surfactant, sodium lauryl sulfate (SLS), was introduced at a concentration of 1800 ppm as a structure-directing agent. Through a self-assembly mechanism, SLS molecules templated the development of macroporous features within the evolving silica matrix. The templated silica nanofluid was subsequently transformed into solid porous particles via spray drying using a two-fluid nozzle atomization system. The spray dryer consisted of a cylindrical drying chamber with a diameter of 15 cm and a height of 50 cm. Atomization was achieved using a two-fluid nozzle with internal diameters of 0.1755 cm and 1.022 cm for the precursor feed and carrier gas channels, respectively. The silica nanofluid was fed at a controlled volumetric flow rate of 100 mL h^{-1} using a syringe pump, while the carrier gas flow rate was maintained at 20 L min^{-1}. Drying was performed at an inlet temperature of 120°C with a constant heating air velocity of 6.7 m s^{-1}, ensuring rapid solvent evaporation and preservation of the templated porous structure. Finally, the resulting porous silica particles were separated from the exhaust stream using a cyclone separator and collected for subsequent amination treatment. The resulting material served as a well-defined porous silica matrix with tailored structural characteristics, suitable for systematic investigation of mass-transfer-limited surface functionalization processes.

Ex-situ surface modification of silica particles using γ-aminopropyltriethoxysilane (APTS) was carried out based on an ultrasound-assisted impregnation strategy. The modifying solution was prepared by mixing APTS, ethanol (Et-OH), and deionized water at an equal volume ratio of 1:1:1, forming a homogeneous amination medium. For each 0.18 g of porous silica particles, a minimum of 1 mL of APTES was employed, resulting in a total immersion volume of 3 mL of modifying solution per 0.18 g of silica to ensure sufficient availability of amination agents. The impregnation process was conducted under ultrasonic irradiation for 6 h, allowing enhanced interaction between the silica surface and the organosilane molecules. Ultrasonic assistance was applied to promote mass transfer, facilitate penetration of APTS into the porous silica network, and suppress diffusion limitations commonly

encountered in conventional impregnation processes. Following impregnation, the modified silica particles were thoroughly washed with ethanol at a volume of 10 mL g^{-1} of silica to remove unanchored or weakly adsorbed amine species. The amine-functionalized silica particles were subsequently dried in an oven at 105°C for 24 h to ensure complete removal of residual solvents and stabilization of the grafted aminopropyl groups. The dried samples were then subjected to physicochemical characterization to evaluate surface properties and amine loading efficiency. For comparative assessment, a conventional impregnation process was also performed under identical conditions but without ultrasonic irradiation. This reference system served as a benchmark to quantitatively evaluate the efficiency gains achieved through process intensification via ultrasound-assisted impregnation.

2.3. Characterization

The morphology of the silica particles was investigated using scanning electron microscopy (SEM) (Hitachi FlexSEM 1000) to assess particle shape, surface features, and size distribution. Quantitative analysis of the SEM images was performed using ImageJ software. For each sample, 200 particles were randomly selected and measured based on the horizontal Feret diameter, ensuring statistically reliable size distribution data. The resulting measurements were subsequently compiled into particle size distribution histograms to evaluate the influence of surface functionalization on particle morphology. The successful ex-situ functionalization of silica particles with organosilane was verified by Fourier transform infrared (FTIR) spectroscopy (Agilent). FTIR spectra were collected over the wavenumber range of 650–4000 cm^{-1} to identify characteristic vibrations of the silica framework as well as newly introduced amine-related functional groups, thereby confirming the chemical grafting of aminopropyl moieties onto the silica surface. The quantity of amine groups immobilized on the silica matrix was determined using thermogravimetric-differential thermal analysis (TG-DTA). Thermal treatment was carried out in two successive stages. In the first stage, physically adsorbed moisture was removed by drying the samples at 105°C until a constant mass was reached after cooling in a desiccator. The second stage involved heating the samples up to 700°C at a constant heating rate of 10°C min^{-1}. This temperature was selected to ensure complete thermal decomposition of grafted amine groups, which has been reported to occur primarily between 150 and 600°C. Throughout the analysis, a continuous flow of nitrogen was applied to suppress oxidative reactions. The mass loss recorded during heating was attributed to the decomposition of surface-bound amine groups and was expressed as the amine loading per gram of silica. The textural properties of the amine-functionalized silica, including specific surface area and pore characteristics, were evaluated using nitrogen adsorption–desorption isotherms (NOVA 1200, Quantachrome). Prior to analysis, all samples were degassed at 120°C under a nitrogen atmosphere for 2 h. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method at relative pressures (P/P_0) below 0.3, while the pore volume and pore size distribution were derived from the desorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) model at relative pressures approaching unity.

The CO_2 adsorption performance of aminopropyl-functionalized silica was evaluated by monitoring the pressure variation of CO_2 within a closed adsorption chamber relative to the inlet gas pressure. The experimental setup consisted of a single adsorption chamber connected to a pressure transducer for real-time measurement of internal pressure changes. An additional pressure transducer was installed at the CO_2 inlet line to enable direct comparison between the inlet pressure and the pressure inside the chamber. Temperature within the chamber was simultaneously monitored using a thermocouple to ensure accurate and dynamic thermal control during the adsorption process. Prior to CO_2 introduction, a known mass of adsorbent was placed inside the chamber, which was then tightly sealed to prevent gas leakage. The system was initially evacuated by closing the gas inlet valve and opening the vacuum pump valve to remove residual gases and impurities, ensuring that the chamber environment was predominantly free of contaminants. Once a stable vacuum condition was achieved, as indicated by the pressure transducer, the vacuum valve was closed. CO_2 gas was subsequently introduced into the chamber by setting the inlet pressure to 1 bar using a pressure regulator and opening the gas inlet valve. After pressure equilibrium between the inlet and the chamber was reached, the inlet valve was closed, and the system was allowed to stabilize until a constant pressure difference was observed. This procedure was repeated at progressively higher inlet pressures, increasing stepwise from 1 to 6 bar. This method enables the evaluation of CO_2 adsorption behavior based on pressure decay profiles, providing insight into the adsorption capacity and dynamic response of the functionalized silica adsorbent.

3. Results and Discussion

The ex-situ surface modification of silica particles via grafting was conducted through two clearly separated stages, namely the synthesis of inert support particles (silica) followed by surface functionalization using an aminopropyl-based organosilane (APTS). As the efficiency of amine grafting is strongly governed by the accessibility of surface-active sites, the synthesized silica support was deliberately engineered to possess a high specific surface area, enabling optimal immobilization of amine functional groups. Porous particle morphology represents a particularly advantageous structural feature for support materials, especially in adsorption-related applications, due to its intrinsically large surface area and enhanced mass-transfer accessibility. Fig. 1(a) presents SEM micrographs illustrating the morphological characteristics of silica particles synthesized using an anionic surfactant (SLS)

template via a consecutive sol-gel spray-drying route. As evidenced by the SEM images, this synthetic strategy successfully produced ordered macroporous silica particles, characterized by a well-defined porous architecture. The formation of macropores on the silica particle surface can be attributed to a self-assembly mechanism involving interactions between surfactant aggregates (micelles) and silica nanoparticles within individual spray droplets. During spray drying, the concentration of SLS exceeded its critical micelle concentration (CMC), promoting the formation of stable micellar structures. These micelles acted as temporary blocking agents, preventing excessive nanoparticle agglomeration during droplet shrinkage, which otherwise drives particle migration toward the droplet center. As solvent evaporation proceeded, the micellar assemblies occupying the interparticle voids were removed concurrently with the solvent phase, leaving behind a network of hollow cavities. This process ultimately resulted in the development of macroporous structures, which are distinctly observable in the SEM micrographs. Through this consecutive sol-gel spray-drying approach, the resulting silica particles exhibited a size distribution ranging from approximately 2.5 to below 12 mm, with an average particle diameter of 5.66 mm and a geometric standard deviation of 1.76 mm, indicating a relatively narrow and well-controlled particle size distribution.

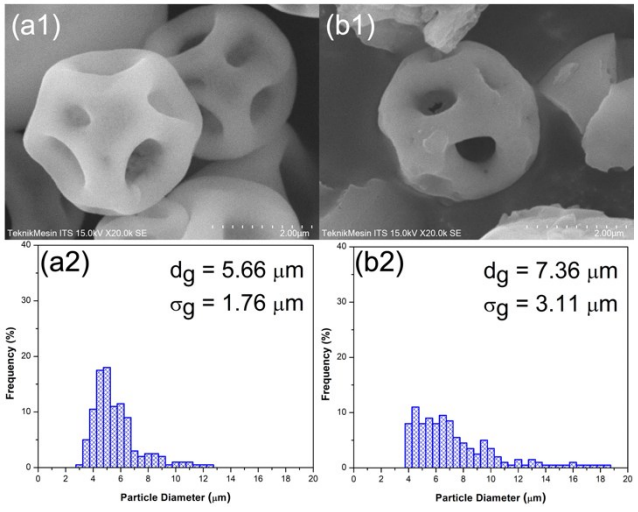

Fig. 1. Morphological evolution and particle size characteristics of silica (a) before and after (b) amine functionalization

In general, the surface modification of silica particles using alkoxy-based ligands such as aminopropyl organosilanes is prone to pore blocking phenomena, primarily arising from partial condensation reactions among modifying agents. This behavior is also evidenced by the experimental results presented in the SEM micrograph in Fig. 1(b), where ex-situ surface modification of macroporous silica particles performed under ultrasound-assisted conditions induces partial coverage of the pore structure. Notably, in the present system, the pore network was not completely obstructed, owing to the macroporous regime of the silica framework, which inherently mitigates severe pore blockage during the modification process. The presence of macropores thus provides a dual advantage: first, it suppresses the extent of pore closure caused by organosilane condensation; second, it facilitates deeper penetration and more effective immobilization of aminopropyl groups throughout the internal pore structure of the silica matrix. Following ultrasound-assisted modification, an increase in the average particle diameter to 7.36 mm, accompanied by a geometric standard deviation of 3.11 mm, was observed. This increase in particle size can be attributed to partial condensation of the modifying agents, which, in addition to contributing to pore coverage, promotes interparticle bridging at the outer surface of the silica particles. Such partial surface condensation may induce particle-particle linking, thereby enhancing the tendency toward agglomeration if not adequately controlled during the modification process. In this context, the application of ultrasonic irradiation plays a critical role by introducing localized shock waves and micro-scale disruptive forces, which homogenize the interaction between silica particles and the modifying agent. These effects effectively reduce the likelihood of extensive interparticle agglomeration by disrupting nascent particle bridges and promoting more uniform surface functionalization. Consequently, the incorporation of ultrasonic assistance during the surface modification process proves to be an effective strategy for minimizing agglomerate formation in amine-functionalized silica particles.

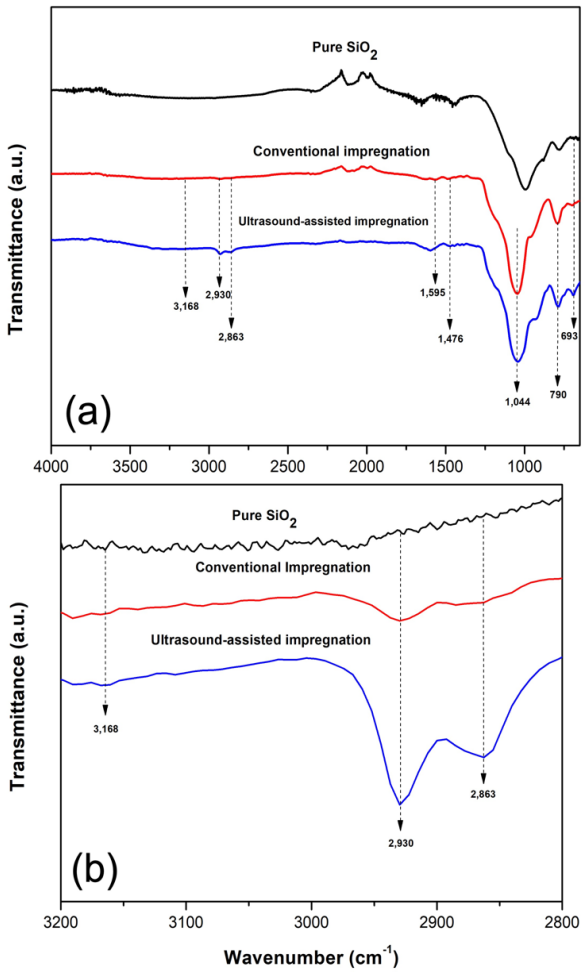

Fig. 2. Comparison of FTIR spectra of amine-modified silica particles prepared using different impregnation strategies

The effectiveness of the post-silanization process was further validated through FTIR spectral analysis, as illustrated in Fig. 2(a), which provides clear molecular-level evidence of amine functionalization on the silica surface. The successful introduction of amine groups is indicated by the emergence of a prominent absorption band at 3168 cm^{-1}, corresponding to the N-H stretching vibration of surface-grafted amines. This observation is reinforced by the appearance of an additional band at 1595 cm^{-1}, which is characteristic of the N-H bending vibration of primary amine groups, collectively confirming the chemical anchoring of aminopropyl moieties onto the silica framework [13]. Further confirmation of organosilane grafting is provided by the presence of alkyl-related vibrational features. The absorption bands detected at 2930 and 2863 cm^{-1} are attributed to the asymmetric and symmetric C-H stretching vibrations of the propyl chains associated with the aminopropylsilane structure. In addition, the band observed at 1476 cm^{-1} corresponds to the C-H bending vibration of aliphatic groups, providing additional evidence for the incorporation of organic functionalities on the silica surface [27,28]. Beyond the emergence of new organic-related bands, significant modifications were also observed in the spectral features associated with the silica matrix itself. The grafting of aminopropyl groups induces measurable perturbations in the siloxane (Si-O-Si) network, as reflected by the shift of the characteristic siloxane band. In pristine silica, this band appears at 991 cm^{-1}, whereas following ultrasound-assisted impregnation, it shifts toward higher wavenumbers, indicating alterations in the local bonding environment due to the formation of covalent Si-O-Si-R linkages. After surface functionalization, the fundamental vibrations of the silica backbone remain clearly identifiable, with characteristic Si-O-Si stretching modes observed at 1044 and 693 cm^{-1}, demonstrating that the structural integrity of the silica framework is preserved. The presence of an additional band at 790 cm^{-1}, associated with Si-O vibrational modes, further confirms the retention of the siloxane network [1,8,12]. Taken together, these spectral features unambiguously demonstrate the successful grafting of aminopropyl groups onto the silica surface while maintaining the intrinsic structural characteristics of the porous silica matrix.

Overall, both post-silanization and in-situ surface modification routes, performed either with or without ultrasonic assistance, exhibit characteristic FTIR bands associated with amine functionalities, confirming the successful introduction of aminopropyl groups onto the silica surface. However, a pronounced difference is observed in the intensity and sharpness of the absorption bands within the wavenumber range of 2800-3200 cm^{-1}, which is attributed to alkyl-related vibrations originating from the alkoxy aminopropyl ligands interacting with surface silanol groups as illustrated in Fig. 2(b). Notably, silica particles modified under ultrasonic irradiation display significantly sharper and more intense absorption bands compared to those obtained via conventional modification without ultrasound. This spectral enhancement qualitatively suggests a higher degree of aminopropyl incorporation, indicating that ultrasonic assistance promotes more effective penetration, diffusion, and anchoring of aminopropyl groups within the internal pore structure of the silica matrix. In conventional modification processes, the diffusion of modifying agents into the internal pore network of the silica support is often hindered by several mass transfer limitations. Among these, the pressure gradient between the pore interior and the external particle surface, as well as the intrinsic viscosity of the modifying solution, represent dominant barriers that restrict the transport of aminopropyl ligands into confined pore spaces. As a result, surface modification tends to be localized predominantly at the outer particle surface, leading to suboptimal utilization of the available internal surface area. The application of ultrasonic irradiation effectively mitigates these diffusion constraints through acoustic cavitation phenomena, whereby the formation, growth, and collapse of microbubbles generate high-energy microjets and intense microstreaming. These effects disrupt the static diffusion boundary layer surrounding the silica particles, enhance local concentration gradients, and facilitate the forced injection of aminopropyl molecules into the interconnected pore network. Furthermore, the presence of a macroporous architecture in the silica support contributes synergistically to diffusion enhancement by reducing internal pore pressure and minimizing the pressure differential between the external surface and the pore interior. This structural feature, in combination with ultrasonic assistance, enables more uniform access of aminopropyl ligands to internal silanol sites. Consequently, a greater fraction of aminopropyl groups can be successfully grafted within the pore structure, leading to a more efficient and homogeneous surface modification process. Collectively, these observations indicate that ultrasound-assisted ex-situ amination significantly enhances the effectiveness of silica surface functionalization by overcoming intrinsic diffusion limitations and maximizing internal amine loading. This process intensification strategy provides a robust and efficient route for producing amine-functionalized silica particles with improved structural accessibility and functional performance.

Pore structure occlusion caused by blocking effects of the modifying agent through localized condensation mechanisms generally exerts a pronounced influence on the final specific surface area of silica particles. In porous materials, the immobilization of active compounds within the pore network inherently leads to a reduction in accessible surface area due to partial pore filling and surface coverage. Prior to surface functionalization, the macroporous silica particles synthesized via a consecutive sol-gel spray-drying route using an anionic surfactant (SLS) as a templating agent exhibited a remarkably high specific surface area of 1174 m^2 g^{-1}. Following aminopropyl modification under ultrasonic assistance, however, the surface area decreased substantially to 426 m^2 g^{-1}. This pronounced reduction, corresponding to approximately 64% loss of the initial surface area, can be attributed to the occupation of the pore network by aminopropyl ligands, which are

immobilized predominantly through physical interactions governed by van der Waals forces [10,15]. The observed decrease in specific surface area is attributed to a pore-blocking mechanism, as evidenced by the reduction in the total pore volume of the silica particles after aminopropyl modification under ultrasonic assistance. This decline is closely associated with structural rearrangement within the pore network, particularly a shift in the pore regime accompanied by a significant decrease in mesopore volume from 1.529 to 0.895 cm^3 g^{-1} after functionalization. The reduction in mesopore volume indicates that a fraction of the mesoporous channels becomes partially obstructed, likely due to the condensation and deposition of aminopropyl groups within the pore walls. Such partial pore blocking is consistent with the grafting mechanism, where silane molecules not only anchor onto the surface but may also accumulate within confined pore spaces. Despite this reduction, the remaining accessible porosity suggests that the functionalization process maintains sufficient pore connectivity, enabling effective mass transfer and contributing to the overall adsorption performance. Such pore filling and partial blockage effectively reduce the number of accessible adsorption sites, particularly within the internal pore structure, thereby lowering the overall surface area. On the other hand, surface modification of silica facilitated solely by physical interactions tends to produce relatively weak bonding compared to chemically driven attachment. Aminopropyl species that do not form strong interactions with surface hydroxyl groups are prone to desorption and may subsequently undergo self-condensation reactions with neighboring aminopropyl molecules through intermolecular interactions. This process can lead to a reduction in the effective amine loading on the silica surface, thereby limiting the functional efficiency of the modified material. Nevertheless, surface functionalization via the ex-situ amination route does not preclude the occurrence of chemical interactions between free surface hydroxyl groups and aminopropyl ligands through condensation reactions. Such interactions can result in the formation of more stable chemical bonds compared to purely physical adsorption. In particular, the interaction between silica surfaces and aminosilanes can give rise to covalent Si-O-Si linkages, formed through electron pair sharing between the oxygen atom of surface hydroxyl groups and the silicon atom of the aminosilane, which simultaneously anchors the terminal amine functionality. The coexistence of both physical immobilization and chemical grafting mechanisms synergistically enhances the functional characteristics of the silica surface. This dual-mode interaction increases the density, stability, and accessibility of amine functionalities, rendering the modified silica surface more selective toward CO_2 molecules through acid–base interactions. Consequently, aminopropyl-functionalized macroporous silica produced via this strategy emerges as a promising candidate for carbon capture applications, combining high amine loading with sufficient structural stability and pore accessibility.

The pronounced reduction in specific surface area can be directly correlated with the qualitative FTIR results, particularly the intensified characteristic amine bands observed after surface functionalization. While FTIR analysis qualitatively demonstrates that ultrasonic-assisted modification plays a significantly more effective role than conventional impregnation in anchoring aminopropyl groups onto the silica surface, quantitative evaluation using TG-DTA measurements provides linear and corroborative evidence supporting this observation. Thermogravimetric analysis reveals that ultrasonic-assisted impregnation enables a substantially higher aminopropyl loading within the silica pore structure, reaching 0.9610 mmol g^{-1} of silica. In contrast, silica particles modified via conventional impregnation without ultrasonic assistance exhibit a markedly lower loading capacity, achieving only 0.4982 mmol g^{-1} of silica, which corresponds to approximately 51.8% of the amine content attained under ultrasonic conditions. This clear disparity quantitatively confirms the superior effectiveness of ultrasonic-assisted impregnation for amine functionalization. The significantly higher aminopropyl loading achieved through ultrasonic assistance indicates a more efficient and homogeneous pore-filling process within the silica support. This behavior suggests that ultrasonic waves act as an additional driving force capable of overcoming diffusion resistance arising from pressure gradients between the internal pore environment and the external particle surface [10,23]. As a result, the mobility of aminopropyl species is markedly enhanced, allowing them to penetrate deeply into the internal pore network rather than remaining predominantly on the external surface. Through this mechanism, ultrasonic-assisted impregnation facilitates the effective and energy-efficient transport of aminopropyl ligands into the internal pores of silica particles, leading to higher functional group density, improved utilization of the porous framework, and overall enhancement of surface modification efficiency.

To evaluate the functionalization efficiency of porous silica in hosting aminopropyl groups, the materials were assessed for CO_2 capture performance. The aminopropyl-modified silica synthesized via ultrasonic assistance exhibited a CO_2 adsorption capacity of 2.2797 mmol g^{-1}, exceeding the commonly reported threshold of 2 mmol g^{-1} for high-performance amine-functionalized adsorbents. In comparison, conventional aminopropyl-grafted mesoporous silica (e.g., SBA-15, MCM-41) typically demonstrates CO_2 uptake in the range of 1.0-2.0 mmol g^{-1} due to diffusion limitations and non-uniform amine distribution, whereas more advanced systems with hierarchical porosity or high amine loading can achieve 2.0-3.5 mmol g^{-1}, often accompanied by increased synthesis complexity and the risk of pore blockage. The superior performance observed in this study can be attributed to a synergistic dual-mechanistic effect: (i) the evolution of the pore structure toward a macropore-dominated regime, which enhances mass transfer and reduces diffusion resistance, and (ii) ultrasonic-induced cavitation, generating localized microjets and shockwaves that promote deeper penetration and more homogeneous distribution of aminopropyl groups within the silica framework. Consequently,

the improved accessibility of active amine sites and more effective CO_2-amine interactions result in enhanced adsorption capacity. Notably, compared to adsorbents prepared via conventional ex situ routes, the present approach demonstrates a clear advantage in balancing amine loading, pore accessibility, and diffusion efficiency, positioning this material among the higher-performing CO_2 adsorbents while maintaining a relatively simple and scalable synthesis strategy.

4. Conclusion

This study demonstrates that ultrasonic-assisted ex-situ amination of macroporous silica particles is a highly effective strategy for enhancing aminopropyl grafting efficiency. Although alkoxysilane-based ligands are intrinsically prone to pore blocking due to local self-condensation reactions, the presence of a well-developed macroporous architecture effectively mitigates extensive pore occlusion. When combined with ultrasonic irradiation, this structural advantage enables deep ligand penetration into the internal pore network through acoustic cavitation, which generates high-energy microjets and intense microstreaming. Beyond cavitation effects, ultrasonic irradiation also enhances molecular vibration of the modifying agent, inducing localized temperature elevation and a simultaneous reduction in solution viscosity. These effects collectively lower mass-transfer resistance and facilitate aminopropyl diffusion toward the internal pore domains. Morphological observations confirm that ultrasonic assistance suppresses excessive particle agglomeration by promoting homogeneous interactions between silica particles and aminopropyl ligands, resulting in a more uniform surface and intrapore functionalization. These morphological findings are strongly supported by FTIR analysis, which reveals significantly sharper and more intense characteristic bands associated with amine and alkyl functionalities in the ultrasonically assisted system compared to conventional impregnation. This spectral enhancement indicates a higher density and more homogeneous distribution of aminopropyl groups throughout the silica framework. Although a substantial reduction in specific surface area is observed after modification from 1174 to 426 m^2 g^{-1} quantitative TG-DTA analysis demonstrates a pronounced increase in amine loading, reaching 0.9610 mmol g^{-1} silica, nearly twice that achieved via conventional impregnation. Importantly, the surface area reduction is primarily attributed to pore filling by aminopropyl ligands rather than structural collapse or degradation of the porous framework. Mechanistically, the improved modification efficiency arises from the synergistic interplay between macroporous morphology and ultrasonic-induced acoustic cavitation. This synergy effectively reduces diffusion barriers, diminishes pressure gradients between external and internal pore regions, and promotes the transport of aminopropyl molecules into the pore interior. These conditions favor the formation of both physical interactions and chemically stable bonds, including covalent linkages between aminosilane ligands and surface silanol groups. Overall, ultrasonic-assisted impregnation emerges as an efficient, scalable, and robust surface-engineering approach for producing amine-functionalized silica particles with high active-site density, controlled morphology, and preserved pore accessibility. These attributes render the resulting material highly promising for application as a selective adsorbent in sustainable CO_2 capture technologies.

Declaration of Competing Interest. The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper

References

[1] H. A. Ajiz, W. Widiyastuti, H. Setyawan and T. Nurtono, Spray-dried porous silica using an anionic surfactant template for advanced photoluminescence support via ultrasound-assisted deposition, *J. Mater. Sci.* (2024).

[2] W. Widiyastuti, H. A. Ajiz, H. Setyawan and T. Nurtono, Electrostatic charge pathway matching interactions between surfactant templates and silica: effects on silica particle morphology and carbon capture performance, *Colloids Surf. A Physicochem. Eng. Asp.* 721 (2025) 137203.

[3] H. A. Ajiz, A. A. Albar, W. Widiyastuti, T. Nurtono, H. Setyawan and I. M. Joni, High surface area silica particles using anionic surfactant template prepared by one-step spray drying system for dye removal application, *Period. Polytech. Chem. Eng.* 66 (2022) 585–595.

[4] S. Y. Lee, W. Widiyastuti, F. Iskandar, K. Okuyama and L. Gradoń, Morphology and particle size distribution controls of droplet-to-macroporous/hollow particles formation in spray drying process of colloidal mixtures precursor, *Aerosol Sci. Technol.* 43 (2009) 1184–1191.

[5] H. A. Ajiz, K. Santoso, J. A. Purnama, W. Widiyastuti, T. Nurtono and H. Setyawan, Preparation of monodisperse ZnO/SiO_2 composite particles using spray drying with an anionic surfactant template and their photoluminescence characteristics, *Adv. Powder Technol.* 34 (2023) 104181.

[6] S. Winardi, L. Qomariyah, W. Widiyastuti, K. Kusdianto, T. Nurtono and S. Madhania, The role of electro-sprayed silica-coated zinc oxide nanoparticles to hollow silica nanoparticles for optical devices material and their characterization, *Colloids Surf. A Physicochem. Eng. Asp.* 604 (2020) 125327.

[7] H. A. Ajiz, L. J. Mawarani, W. Widiyastuti and H. Setyawan, High-stability foam of silica nanofluid to overcome liquid loading in enhancing natural gas production, *IPTEK J. Technol. Sci.* 32 (2021) 23.

[8] S. Muljani, H. Setyawan, G. Wibawa and A. Altway, A facile method for the production of high-surface-area mesoporous silica gels from geothermal sludge, *Adv. Powder Technol.* 25 (2014) 1593–1599.

[9] W. Widiyastuti, M. F. Rois, N. M. I. P. Suari and H. Setyawan, Activated carbon nanofibers derived from coconut shell charcoal for dye removal application, *Adv. Powder Technol.* 31 (2020) 3267–3273.

[10] H. A. Ajiz, W. Widiyastuti, H. Setyawan and T. Nurtono, Amine-functionalized porous silica production via ex- and in-situ method using silicate precursors as a selective adsorbent for CO_2 capture applications, *Heliyon* (2024) e26691.

[11] H. A. Ajiz, R. P. Ardiansyah, M. S. K. R. Dwiatmaka, H. Setyawan, T. Nurtono and W. Widiyastuti, Silica surface modification using cellulose as a renewable organosilane derived from coconut coir fiber for carbon capture, *Results Eng.* (2024) 103060.

[12] H. A. Ajiz, W. Widiyastuti, H. Setyawan, T. Nurtono and others, Direct surface modification of a silica-based adsorbent for CO_2 capture from coir fibers dissolved in a sulfur-free alkali-urea system, *Adv. Powder Technol.* 36 (2025) 104912.

[13] H. A. Ajiz, W. Widiyastuti, H. Setyawan, S. Muljani, A. S. Suryandari and N. K. Erliyanti, Unveiling the role of cellulose solvent systems in direct and sustainable silica amination: a new pathway beyond aminopropyl agents, *Konversi* 14 (2025) 37–44.

[14] B. Qiao, T. J. Wang, H. Gao and Y. Jin, High density silanization of nano-silica particles using γ-aminopropyltriethoxysilane (APTES), *Appl. Surf. Sci.* 351 (2015) 646–654.

[15] H. Y. Huang, R. T. Yang, D. Chinn and C. L. Munson, Amine-grafted MCM-48 and silica xerogel as superior sorbents for acidic gas removal from natural gas, *Ind. Eng. Chem. Res.* 42 (2003) 2427–2433.

[16] J. T. Anyanwu, Y. Wang and R. T. Yang, Amine-grafted silica gels for CO_2 capture including direct air capture, *Ind. Eng. Chem. Res.* 59 (2020) 7072–7079.

[17] S. Cui, S. Yu, B. Lin, X. Shen, X. Zhang and D. Gu, Preparation of amine-modified SiO_2 aerogel from rice husk ash for CO_2 adsorption, *J. Porous Mater.* 24 (2017) 455–461.

[18] N. Hao, K. W. Jayawardana, X. Chen and M. Yan, One-step synthesis of amine-functionalized hollow mesoporous silica nanoparticles as efficient antibacterial and anticancer materials, *ACS Appl. Mater. Interfaces* 7 (2015) 1040–1045.

[19] R. Ullah, M. Atilhan, S. Aparicio, A. Canlier and C. T. Yavuz, Insights of CO_2 adsorption performance of amine impregnated mesoporous silica (SBA-15) at wide range pressure and temperature conditions, *Int. J. Greenh. Gas Control* 43 (2015) 22–32.

[20] S. Moon and K. J. Lee, Simultaneous control of size and surface functionality of silica particle via growing method, *Adv. Powder Technol.* 28 (2017) 2914–2920.

[21] C. Chen, S. Zhang, K. H. Row and W. S. Ahn, Amine–silica composites for CO_2 capture: a short review, *J. Energy Chem.* 26 (2017) 868–880.

[22] Z. Wu, S. Tagliapietra, A. Giraudo, K. Martina and G. Cravotto, Harnessing cavitational effects for green process intensification, *Ultrason. Sonochem.* 52 (2019) 530–546.

[23] S. V. Sancheti and P. R. Gogate, A review of engineering aspects of intensification of chemical synthesis using ultrasound, *Ultrason. Sonochem.* 34 (2017) 540–560.

[24] Y. Yao, Enhancement of mass transfer by ultrasound: application to adsorbent regeneration and food drying/dehydration, *Ultrason. Sonochem.* 27 (2016) 530–546.

[25] L. P. Ferraz and E. K. Silva, Pulsed electric fields and ultrasound for enhanced mass transfer: a review of extraction and drying in food processing, *ACS Food Sci. Technol.* (2025).

[26] H. L. Yeh and J. J. Juárez, Ultrasound-enhanced diffusion and streaming of colloids in porous media, *Exp. Therm. Fluid Sci.* 121 (2021) 110282.

[27] A. S. Suryandari, T. Nurtono, W. Widiyastuti and H. Setyawan, Hydrophobic modification of sulfonated carbon aerogels from coir fibers to enhance their catalytic performance for esterification, *ACS Omega* 8 (2023) 27139–27145.

[28] S. Susanto, T. Nurtono, W. Widiyastuti, M. H. Yeh and H. Setyawan, Controlling N-doping nature at carbon aerogels from biomass for enhanced oxygen reduction in seawater batteries, *ACS Omega* 9 (2024) 13994–14004.