



Research article

Amine-functionalized porous silica production via ex- and in-situ method using silicate precursors as a selective adsorbent for CO₂ capture applications

Hendrix Abdul Ajiz, W. Widiyastuti^{*}, Heru Setyawan, Tantular Nurtono*Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya, 60111, Indonesia*

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ABSTRACT

A comparison of the amine-modified silica particle's characteristics via ex- and in-situ routes and their application as a CO₂ gas adsorbent is reported. Modifying silica particles via ex-situ involves two separate steps: forming porous silica particles with sodium lauryl sulfate (SLS) as a template and impregnation using ultrasound assistance. In contrast to ex-situ modification, in-situ modification of silica particles is carried out in one step by mixing directly between the silica source and the modifying agent. Controlling the characteristics of modified silica particles via in-situ is carried out by adding an SLS template removed simultaneously with particle formation to increase the surface area and porosity. Increasing the SLS template concentration shows a linear relationship between increasing particle surface area and amine loading. However, two different modification routes exert a direct influence on aminopropyl distribution. Silanization via in-situ which involves a simultaneous condensation reaction produces a higher amine loading reaching 1.2845 mmol/g of silica than via ex-situ which is only 0.9610 mmol/g of silica. The amount of aminopropyl that can be grafted on the silica surface shows a linear relationship to the quantity of CO₂ gas adsorption capacity. Amine-modified silica particles obtained the highest adsorption capability via the in-situ route with an SLS 3 CMC template of 2.32 mmol/g silica at an operating pressure of 6 bar.

1. Introduction

Nanoparticle synthesis technology research has developed rapidly in the last few decades. Silica-based nanoparticles are one of the most widely applied nanomaterials in several fields ranging from environmental to energy issues. Silica is widely applied as an absorbent-adsorbent material, catalyst support, membrane, and slow-release drug delivery material. Besides having good mechanical properties and non-toxicity, silica-based functional materials can be modified to improve their performance in specific applications [1–7]. Modifying silica is carried out by grafting active functional groups on the surface of the support material either physically or chemically [8–11]. Amine-modified silica is a further modified material widely used as a functional material through various mechanistic routes [12]. Amino silane is one of the functional groups that can be grafted onto the silica surface to increase its selectivity. The grafting of amine functional groups on the silica surface can be obtained from organo-silanes, one of which is γ -aminopropyltriethoxysilane (APTS) [13].

^{*} Corresponding author.

E-mail address: widi@chem-eng.its.ac.id (W. Widiyastuti).

Modifying silica particles with amine groups can be done by ex- and in-situ modification [14,15]. The method of grafting amine groups by the ex-situ is carried out separately between forming the support material, followed by the physical and chemical modification stages using amino silane [9]. One method that is widely used during the ex-situ process is direct condensation in toluene (DCT) by refluxing silica particles into the amino silane/toluene mixture at its boiling point [12,16]. Apart from using reflux, the process of developing amine groups can also be carried out by impregnation, which is then followed by thermal treatment. So far, the impregnation process requires that the morphology of the support material has porous characteristics to accommodate more active material that can be carried. On the other hand, the ex-situ method is claimed to be inefficient because it involves two separate stages and requires an extended processing time with relatively small amounts of amino silane that can be carried on the support material with uneven distribution. Modification through ex-situ generally cannot develop high parts of amino silane because silica condensation occurs first and stops when the particles have formed, causing a decrease in the activity of the silanol groups to interact with the amino silane groups at a later stage [16,17].

In contrast to ex-situ, surface modification through the in-situ method, carried out simultaneously with forming silica particles, can produce amine-modified silica particles in one-step synthesis. The mechanism of grafting amine groups on the silica surface involves three possibilities that can occur based on the number of replaceable hydroxyl groups. The hydroxyl group in APTS has three parts that form bonds with silanes, showing that one hydroxyl group can be bonded to one hydrogen atom on the silica surface to form H₂O as a by-product during condensation reaction so that silanes will bond to three oxygen atoms on the silica surface. Replacing hydroxyl groups with organo-silanes can produce different structures called monodentate, bidentate, and tridentate [13]. The difference in the amine structure that can be grafted is one of the factors that the condensation reactions that occur separately between organo-silane and silica can cause an uneven distribution of amine groups on the silica surface. Therefore, one can produce the amine-modified silica with an even distribution by reacting together the silica and amine sources so that the condensation reaction can occur simultaneously. Until now, the grafting of amine groups on silica through the in-situ mechanism often involves changing the liquid phase to a gel due to the speed of the condensation process of silica and APTS as an amine source. The high condensation reaction rate between APTS and the silica source causes the resulting particle morphology challenging to control. Therefore, the in-situ mechanism is rarely maintained in a stable colloidal phase because it constantly forms aggregates between the particles. The synthesis of amine-modified nano-silica is still limited to the use of tetraethyl orthosilicate (TEOS) as a source of silica because the speed of the condensation reaction is relatively slow so that a catalyst such as ammonium hydroxide (NH₄OH) is still needed in alcoholic conditions as a source of hydroxyl groups [10, 18]. In contrast to sodium silicate (Na₂SiO₃), which already has hydroxyl groups without requiring special treatment, the condensation reaction speed directly proportional to APTS makes it more synthesized in the form of modified silica gel [19].

The synthesis routes of amine-modified silica particles between ex- and in-situ methods seem different at first glance. Still, they are relatively the same when viewed from the mechanism of particle formation. The sol-gel mechanism is one of the methods for forming silica particles that can be applied to both types of routes, but sufficient time is required to produce a strong gel structure. The consecutive sol-gel spray drying method is an alternative because it can produce particles with a short residence time at moderate temperatures [20]. Particle formation using spray drying, which follows the one droplet to one particle (ODOP) rule, can produce relatively free agglomeration [21]. Controlling the morphology of silica particles using the spray drying method can be carried out by adjusting the precursor concentration and operating conditions of the spray drying [22,23]. For specific morphology, such as porous, a chemical compound can be added that functions as a template to optimize pore formation [24–27]. Using soft templates such as surfactants, which are soluble in polar and non-polar solvents, initiates the synthesis of porous silica in one step [28–30]. The formed surfactant molecule aggregation will evaporate with the solvent in the spray drying system, leaving a hollow structure on the particle surface [1]. Synthesis of porous silica using soft templates with the consecutive sol-gel spray drying method is a promising alternative for producing support materials in the ex-situ route. The consecutive sol-gel spray drying method also allows it to be applied to the in-situ route with several adjustments, especially in controlling precursor conditions, so that agglomeration does not occur and is stable in the colloid phase.

In this study, we compared the synthesis of amine-modified silica particles between ex- and in-situ methods using Na₂SiO₃ as a silica source and APTS as an amine source. The consecutive sol-gel spray drying method was used to form support material for the ex-situ modification and amine-modified silica particles for the in-situ method in one step, which has not been widely reported in previous studies. Sodium lauryl sulfate (SLS) is used to increase the particles' porosity and surface area. In the ex-situ method, modifications were made using ultrasound-assisted impregnation to increase the amount of amine that can be carried on the silica particles. In contrast, in the in-situ modification, a low concentration of Na₂SiO₃ was chosen to control the rate of condensation between silica and APTS so as not to form agglomeration in the silicate-amino silane precursors. Particles obtained in each modification method were characterized to determine the characteristics and differences in the mechanisms occurring in amine-modified silica particles' formation phenomenon. The application of amine-modified silica particles in each method was also investigated to determine the effect of the particle characteristics on its performance as a selective adsorbent for CO₂ gas.

2. Experimental

2.1. Materials

The material used in this study was sodium silicate (Na₂SiO₃) with a silica concentration of 27% and a ratio of SiO₂:Na₂O of 3.3 standard reagent p.a. purchased from Merck. Flotrol-007 cationic resin, HCl standard reagent p.a. 37% purchased from Mallinckrodt, KOH standard reagent p.a. purchased from Merck, technical standard SLS anionic surfactant supplied from CV. Citra Sari Kimia, Indonesia. γ -aminopropyltriethoxysilane (APTS) 99% standard reagent p.a. purchased from Sigma Aldrich. Ethanol absolute

(C₂H₅OH) standard reagent p.a. purchased from Merck. Ultra-high purity CO₂ gas was supplied from CV. Sumber Gas, Indonesia. All materials obtained are used without going through a further purification process. The water used during synthesis is demineralized water pH 5 purchased from UD. Sumber Ilmiah Persada, Indonesia.

2.2. Synthesis of amine modified silica particles by the ex-situ method

Surface modification of silica particles with amines through the ex-situ method is carried out in two separate stages, namely the formation of particles, which is then followed by modification of the particle surface. Briefly, Na₂SiO₃ was dissolved in demineralized water at 60 °C with a concentration of 0.7 M SiO₂. The Na₂SiO₃ solution was processed using a cation exchanger to replace Na⁺ ions with H⁺ ions. The ion exchange process was carried out in batches using a magnetic stirrer for 30 min until active silicic acid (Si(OH)₄) with a pH of 2 was obtained. 0.1 M KOH solution was added dropwise into silicic acid as a catalyst to induce the formation of silica nanoparticles until pH 10 was obtained. After obtaining silica nanofluid, SLS anionic surfactant was added with various concentrations based on the critical micelle concentration value (1, 2, and 3 CMC). Silica particles were obtained through a spray drying process using two-fluid nozzles as atomizers. The spray dryer instrumentation used has chamber dimensions with a diameter of 15 cm and a height of 50 cm. The two-fluid nozzles used as atomizers have inside diameter (ID) specifications for the feed precursor and tube carrier gas of 0.1755 cm and 1.022 cm, respectively. The cyclone is used as a separator unit to separate the silica particles obtained and then accommodated in the particle collector. Silica nanofluid was fed using a syringe pump with a volumetric flow rate of 0.1 L/h. Several other parameters in the spray drying process are also determined during the spray drying process, such as the volumetric carrier gas rate of 1200 L/h and the drying temperature of 120 °C with a constant linear heating air velocity of 6.7 m/s.

Modification of silica particles using APTS through the ex-situ method was carried out using the principle of the ultrasound-assisted impregnation method. The modifying agent solution consists of a mixture of APTS: Et-OH: H₂O with a volume ratio 1:1:1 for each mixture. For every 0.18-g of silica particle, at least 1 mL of APTS is needed so that if in the system, every 0.18-g of silica particle will be immersed in 3 mL of a modifying agent solution. The impregnation process was carried out with the help of ultrasonic waves for 6 h, followed by a washing step using Et-OH 10 mL/g of silica. The washing process aims to remove the amine groups that the silica particles cannot penetrate. The amine-modified silica particles were then dried in an oven at 105 °C for 24 h and then characterized to determine the characteristics of the resulting particles. As a comparison to show the effect of using ultrasonic waves on increasing the quantity of aminopropyl that can be embedded in silica particles, ex-situ surface modification of the silica particles was also carried out using conventional impregnation principles. The modification process is carried out by immersing a several of silica particles in the modifying agent solution for 6 h without the help of ultrasonic waves or stirring.

2.3. Synthesis of amine modified silica particles by the in-situ method

Suppose the previous procedure uses an ultrasonic wave-assisted impregnation method to expand the number of amine groups on silica particles using physical or chemical bonds. In that case, the silanization procedure directly involves a chemical condensation reaction known as chemical grafting. To be able to compare the number of amine groups that can be grafted, the same ratio as the previous procedure used the composition of the modifying agent APTS: Et-OH: H₂O with a volume ratio of 1:1:1. For every 30 mL of 0.1 M sodium silicate as a precursor requires 1 mL of APTS. The mixing process between sodium silicate and the modifying agent is carried out after it undergoes pre-condensation by stirring for 10 min before mixing it into the sodium silicate. The purpose of stirring the modifying agent before mixing it into the silicate precursor is to control the speed of the condensation reaction so that it does not form an agglomeration of particles that can precipitate. The mixing process between sodium silicate and the modifying agent was carried out by rapid stirring and adding 1 M HCl solution drop by drop until a pH of 11 was obtained, followed by sonication for 30 min to minimize the formation of particle agglomeration. During this process, silica and APTS will undergo a condensation reaction simultaneously so that the resulting silica particles will automatically bind to the amine group at the end of the silanol group. After sonication of the silica-amine precursor solution, SLS surfactant was added with various concentrations of 1, 2, and 3 CMC to improve the morphological characteristics of the resulting particles. The particle formation process was carried out using the spray drying method at predetermined conditions at a temperature of 120 °C, a volumetric feed rate of 0.1 L/h, a volumetric carrier gas rate of 1200 L/h, and a linear drying air velocity of 6.7 m/s.

2.4. Characterization

The morphology of the silica particles was visually analyzed using a Hitachi FlexSEM 1000 Scanning Electron Microscopy (SEM). The results of the SEM analysis were processed using ImageJ software to determine the size distribution of the resulting silica particles. A total of 200 particles for each variable were determined by using the horizontal diameter ferret method, whether they included donut-shaped or spherical particles, which were then made into a histogram of the particle size distribution. The success of the modification process using organo-silane in the ex- and in-situ method was carried out using the Fourier Transform Infrared (FTIR: Agilent) Spectroscopy test. FTIR analysis was carried out at a wavenumber of 650-4,000 cm⁻¹. To express the quantity of amine that is successfully embedded or grafted, heating treatment is used with the TG-DTA principle. Heating treatment is carried out in two stages. Where the first stage aims to determine the moisture content in the sample by heating several samples at a temperature of 105 °C for a specific time, then cooling them in a desiccator and weighing them until a constant weight is obtained. Then, proceed with the second heating stage to a temperature of 700 °C with a temperature increase rate of 10 °C/min. The temperature of 700 °C was chosen because, in previous studies, the profile of mass reduction due to amine decomposition occurred at temperatures of 150 °C–600 °C < T

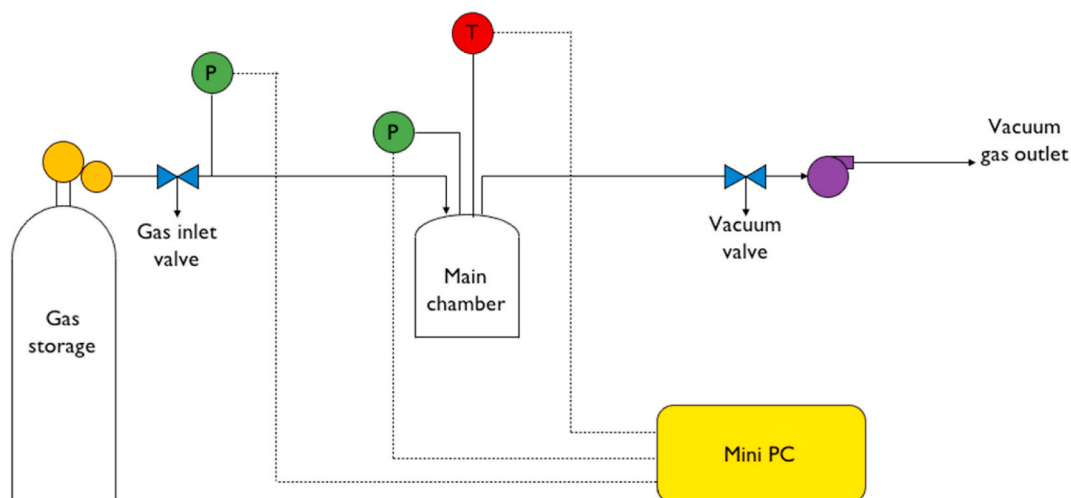


Fig. 1. Schematic of the batch adsorber column instrument.

< 700 °C and to ensure that the amine could decompose completely. During the heating process up to 700 °C, it is carried out with a flow of nitrogen gas to prevent sample oxidation due to the presence of oxygen in the system. After the muffle furnace temperature drops to room temperature, the sample is then weighed to obtain the mass reduction that occurs and is expressed as the mass of amine contained in the sample per gram of silica. The amine functional groups grafted on the silica surface can be determined using Eq. (1) as follows:

$$\text{Loading amine} = \frac{(A - B) \text{ mg}}{MW \text{ aminopropyl} \frac{\text{mg}}{\text{mmol}} \times m_{\text{silica}} (\text{gram})} \left(\frac{\text{mmol aminopropyl}}{\text{gram silica}} \right) \quad (1)$$

Where A is the weight of water adsorbed free silica (mg), B is the weight of silica after being furnace at a temperature of 700 °C, MW aminopropyl is the relative molecular weight of γ -aminopropyltriethoxysilane (mg/mmol), and m_{silica} is the initial weight of silica as a basis for calculation (gram). The surface area of the amine-modified silica particles was determined quantitatively using an isothermic nitrogen adsorption-desorption method (NOVA 1200, Quantachrome). Before analysis, samples of silica particles were degassed at 120 °C under nitrogen gas for 2 h. The Braunaauer-Emmett-Teller (BET) method determines the specific surface area at a relative pressure <0.3. At the same time, the pore volume is calculated from the adsorption-desorption profile data of the isothermal desorption branch using the Barret-Joyner-Halenda (BJH) theory at a relative pressure close to 1. 0.

The performance of amine-modified silica particles as a carbon dioxide adsorbent was tested by measuring the change in CO₂ gas pressure in the chamber containing the adsorbent against the inlet CO₂ gas pressure. Performance tests are carried out using a single chamber connected to a pressure transducer to measure pressure changes that occur in the chamber as illustrated in Fig. 1. At the CO₂ gas inlet to the chamber, a pressure transducer is also installed to compare the pressure between the CO₂ gas entering the chamber and the change in CO₂ gas pressure in the chamber. Temperature measurements are also carried out inside the chamber which can be observed dynamically using a thermocouple. Before CO₂ gas is supplied, the adsorbent sample is put into the chamber with a certain weight and then closed tightly to prevent gas leaks which can reduce the pressure in the chamber significantly. For initial conditioning, the pressure in the chamber is reduced to vacuum by closing the inlet gas valve and opening the vacuum pump valve to remove other gas impurities so that it is assumed that the chamber will only be filled with CO₂ gas. After the pressure transducer shows vacuum pressure in the chamber, the vacuum pump valve is closed. The inlet gas pressure is set to 1 bar on the regulator and flows into the chamber by opening the inlet gas valve. After the inlet gas and chamber pressures are the same, then the inlet gas valve is closed and observed for a few moments until the pressure difference value between the inlet gas and chamber is constant. After obtaining a constant pressure difference value, then the CO₂ gas pressure is increased to 2 bar and the procedure above is repeated by adjusting the inlet gas pressure to 6 bar.

3. Result and discussion

3.1. Amino-functionalized silica particle characteristics via ex-situ modification route

Surface modification of the silica particles using the ex-situ method was carried out in two separate stages: forming the particles, followed by surface modification using APTS. The characteristics of the particles synthesized as a support material must have a high surface area to accommodate the amine groups so that they can be carried on the surface of the particles. The morphology of porous particles is one type of particle shape that can be applied as a support material because it has a high surface area. Fig. 2 shows the effect of adding SLS surfactant with varying concentrations on the morphology of the resulting silica particles after drying using a spray

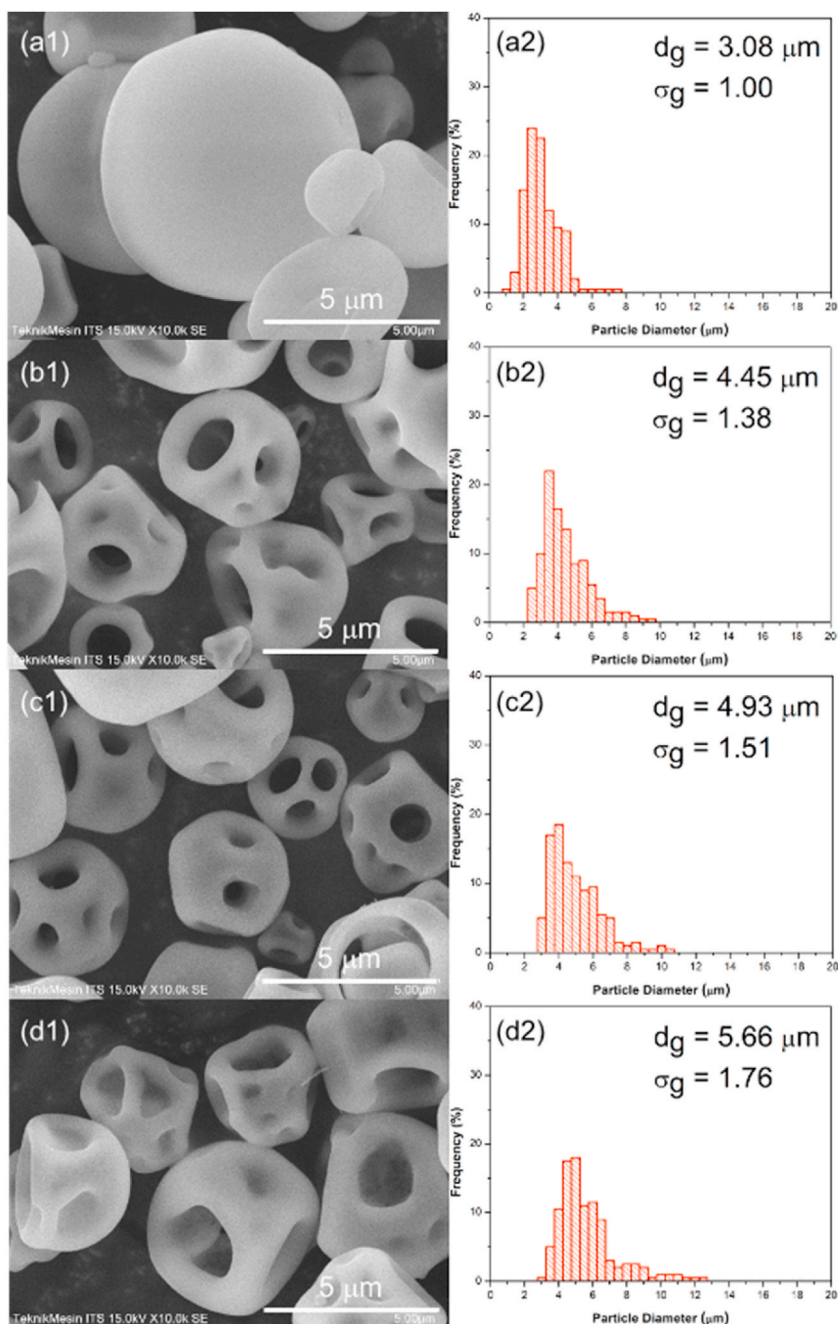


Fig. 2. SEM image and size distribution of silica particles with the addition of SLS at various concentrations (a1-a2) 0, (b1-b2) 1, (c1-c2) 2, and (d1-d2) 3 CMC.

dryer. Fig. 2(a1) shows the SEM image of silica's morphology without the addition of SLS surfactant. Based on the SEM images, the resulting silica particles follow the one droplet to one particle (ODOP) rule by forming two types of morphology, which can be categorized in spherical and donut shapes. The size distribution of silica particles before the addition of SLS surfactant showed distribution in a relatively narrow range of distribution gaps with particle sizes ranging from 1.25 μm to less than 8 μm with an average diameter of 3.08 μm as shown in Fig. 2(a2). The narrow gap in the size distribution of silica particles without adding SLS is also indicated by the geometric standard deviation of 1.00.

The different morphology of silica particles is shown when SLS is added to the silica precursor in various SLS concentrations, as depicted in Fig. 2(b1-d1). A macroporous structure on the silica particle surface is formed due to solvent evaporation followed by template removal in the form of surfactant molecules aggregation or micelles, which then leaves a hollow structure. The macroporous

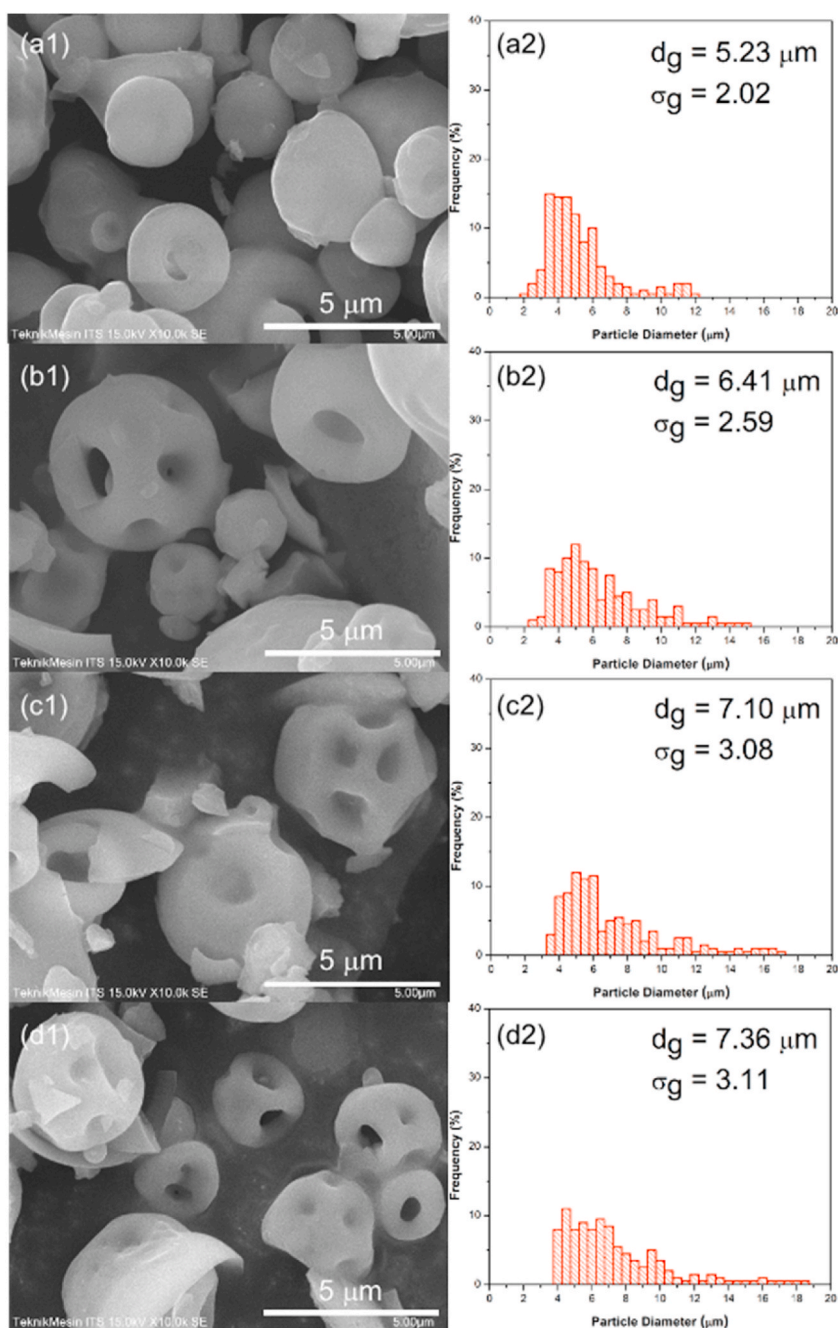


Fig. 3. SEM image and size distribution of amine-modified silica particles with the addition of SLS at various concentrations (a1-a2) 0, (b1-b2) 1, (c1-c2) 2, and (d1-d2) 3 CMC through the ex-situ route.

structure on the silica particles surface can show the aggregation pattern of surfactant molecules formed in the silica-surfactant precursor. The existence of a macroporous structure with a symmetrical round shape indicates that the aggregation of surfactant molecules exhibits a spherical shape. The electrostatic effect on SLS surfactants also plays a role in forming macroporous structures on silica particles. Generally, silica has a negative surface charge when it is in alkaline conditions. This also synergizes with the electrostatic effect produced by the anionic surfactant SLS. The high similar charge on the surface of the silica nanoparticles, which also interacts with the surfactant molecules, gives a greater repulsive force. The higher the repulsive force exerted between the nanoparticles in the droplet causes the silica nanoparticles to move away from each other. However, when the amount of solvents evaporates and is followed by a decrease in droplet size, the silica nanoparticles will move toward the center of the droplet as the droplet volume decreases. In the droplet shrinkage process, which causes a reduction in droplet dimensions, a condition will be reached where

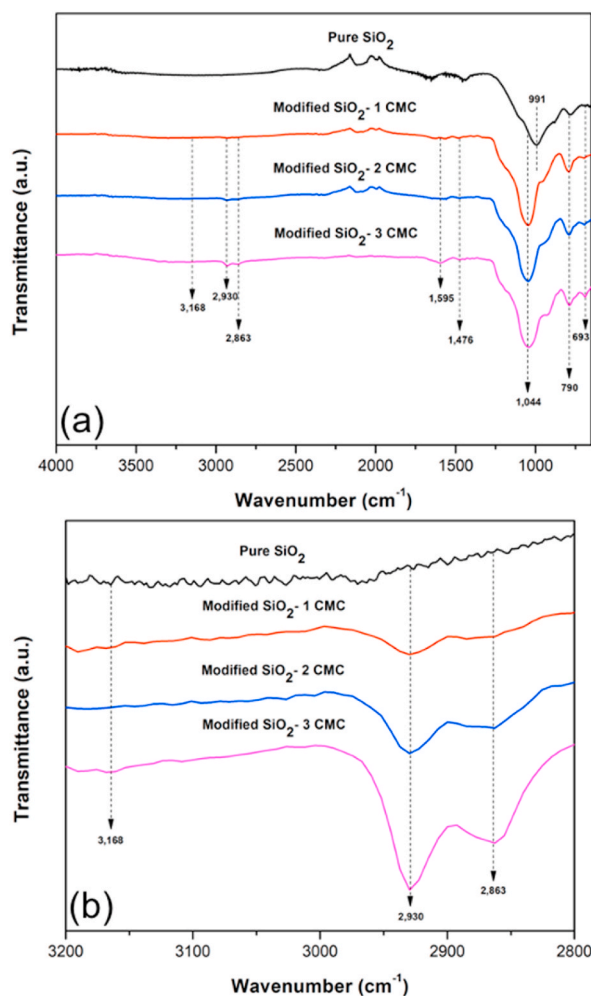


Fig. 4. (a) Long and (b) short wavenumber FTIR spectra of amine-modified silica particles with various SLS concentrations using the ex-situ method.

the aggregation of surfactant molecules will be trapped between the silica nanoparticles. Through that mechanism followed by the template removal, which evaporates with the solvent a pore structure will form on the surface of the silica particles. Increasing the SLS concentration added to the silica precursor has more macroporous structures with better distribution in each particle unit formed. The increasing quantity of macroporous structures formed on the silica surface causes an increase in the average diameter of the silica particles from 4.45 μm to 5.66 μm as shown in Fig. 2(b2-d2). The increase in the diameter of the silica particles was also followed by an increase in the geometric standard deviation from 1.38 to 1.76, which showed a more polydisperse size distribution than when the SLS concentration was lower.

The morphology of the silica particles after being modified using APTS with ultrasound-assisted did not show significant changes to the morphology of the particles before modification, as depicted in Fig. 3(a1-d1). For particles with a porous morphology, it can be clearly seen that the modifying agent makes an effort to close the pores by forming a layer at the edge towards the center of the pore. Pore closure by the modifying agent can occur due to the condensation reaction by the modifying agent, which takes place during the modification process. However, the macroporous structure formed on the particle surface can minimize total pore closure by the modifying agent so that the characteristics of the porous material can be maintained. As a result of the separate condensation reaction between the modifying agent and silica causes a layer to form on the silica surface, which can bind other particles and form agglomeration. The formation of particle agglomeration after silanization can be seen from the change in particle size distribution to become more significant as shown in Fig. 3(a2-d2). The average particle size increased by 46.98% from the original particle size before modification using APTS. The highest percentage increase in particle size occurred in particles without adding the SLS template at 69.81% and decreased linearly to 30.04% in silica particles with the SLS 3 CMC template. It shows that particles with a smaller size tend to experience a more dominant agglomeration process than particles with a larger size. Therefore, the formation of particle agglomeration after modification causes the particle size distribution to become more non-uniform, potentially reducing the particles' overall surface area.

The success of the modification using the ex-situ method can be confirmed by the FTIR spectra, as shown in Fig. 4(a). The presence

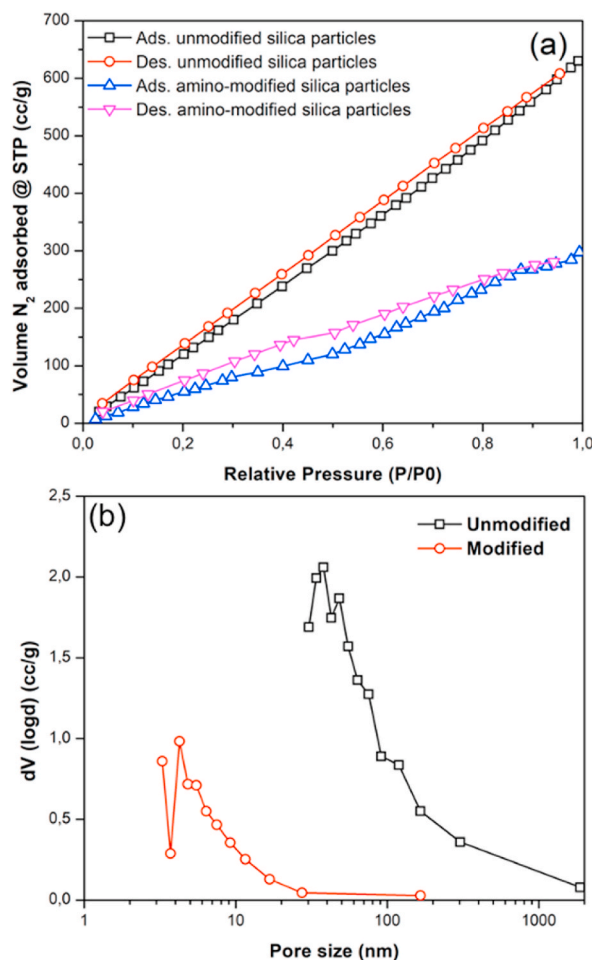


Fig. 5. (a) N_2 adsorption-desorption isotherm and (b) mesopore size distribution of silica particles with the addition of 3 CMC SLS before and after modification using aminopropyl via ex-situ route.

of amine functional groups on the silica surface is indicated by a peak at wave number $3,168\text{ cm}^{-1}$, which can be attributed to the amine stretching (N–H stretching). The appearance of the characteristic amine peaks on the silica surface is also reinforced by the presence of a peak at wave number $1,595\text{ cm}^{-1}$, which can be attributed to the bond of the primary amine (N–H bend). Besides being marked by the presence of characteristic amine peaks, the success of carrying organo-silanes on the surface of silica particles is also indicated by the presence of distinct peaks of alkane groups. The appearance of peaks at wave numbers $2,930$ and $2,863\text{ cm}^{-1}$ can be attributed to the stretching vibration of the –CH bond associated with the –NH group as shown in Fig. 4(b). The appearance of alkane groups on the surface of the silica particles is also indicated by a peak at wave number $1,476\text{ cm}^{-1}$, which can be attributed to the –CH group of aminopropyl. Besides coming from aminopropyl, other peaks in the FTIR spectra show characteristic peaks associated with silica. The emergence of interactions between the embedded amine groups and silica causes a shift in the siloxane peak. Before the ultrasonic wave-assisted impregnation process was carried out, the characteristic peak of the siloxane groups in silica was shown at wave number 991 cm^{-1} and shifted to a higher wave number after being penetrated by aminopropyl. After being attached to the aminopropyl group on the siloxane functional group (Si–O–Si or O–Si–O), the characteristics of silica particles appeared sequentially at wavelengths of $1,044$ and 693 cm^{-1} . The presence of a peak at 790 cm^{-1} also confirms the characteristics of the siloxane group, which can be attributed to the Si–O bond vibration.

The effect of ultrasonic wave-assisted ex-situ modification on the physical characteristics of particles, including surface area and mesopore size distribution, is shown by the N_2 isothermal adsorption-desorption profiles of silica particles with the SLS 3 CMC template as shown in Fig. 5(a). Silica particles before and after the modification step show a type IV curve characterized by type H2 hysteresis at $P/P_0 \geq 0.3$, indicating mesoporous characteristics. Silica particles, after being modified using amine, showed that the amount of N_2 gas adsorbed on the surface of the particles had a lower volume compared to the before being modified. The decrease in the amount of N_2 gas that can be adsorbed on the silica particles' surface after being modified indicates a reduction in the particles' surface area. The decrease in the surface area of the particles can be due to the pore filling by the amine functional group during the modification process, thereby reducing the pore volume and mesoporous distribution range of silica particles as a support material as

Table 1
Characteristics of amine-modified silica particles using the ex-situ method.

SLS Concentration (CMC)	Specific surface area (m ² /gram)		Amine loading (mmol/gram silica)
	Unmodified	Modified	
0	248.410	174.222	0.4525
1	370.903	238.499	0.8299
2	688.831	246.172	0.8984
3	1,174.225	426.419	0.9610

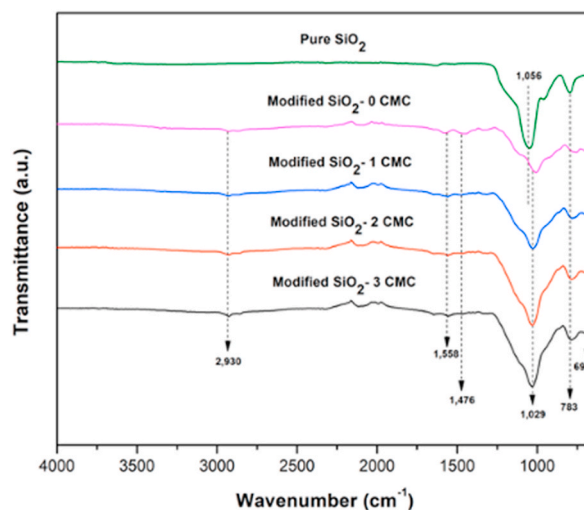


Fig. 6. FTIR spectra of amine-modified silica particles with various SLS concentrations using the in-situ method.

shown in Fig. 5(b). Before being modified using amino, the silica particles had a mesopore volume of 1.210 cc/gram and decreased to 0.363 cc/gram after modification, this shows a significant decrease in mesopore volume reaching 70% of the original. The decrease in the mesopore volume of silica particles before and after modification was also accompanied by a decrease in the mesopore volume fraction of the particles. Before modification, silica particles had a mesopore volume fraction of 97.27% and decreased to 78.88% after modification using aminopropyl. The decrease in mesopore volume fraction that occurs during the modification process is due to the closure of the mesopore structure by self-condensation of aminopropyl. However, the volume fraction of mesoporous particles can be maintained at more than 75% because the pore structure is formed in the macroporous regime. This causes silica particles modified via the ex-situ route to not experience a total reduction in the mesoporous and micropore regimes with smaller volumes. It shows that the presence of a macroporous structure on silica particles can minimize total pore blocking, which causes a significant decrease in the surface area of the particles. It follows the SEM image, which shows that the presence of the macroporous structure can maintain its shape even though it has experienced a reduction in macropore size due to APTS condensation during the modification process.

The effect of adding SLS surfactant on the silica particle characteristics before and after modification using aminopropyl is summarized in Table 1. Based on the results obtained, the addition of SLS to the silica precursor contributes to increasing the silica particle's surface area which can be attributed to the interaction of surfactant molecules which act as a template to form a pore structure on the particle's surface. An increase in SLS concentration has a linear relationship with an increase in the surface area of the silica particles produced. Before undergoing modification using aminopropyl, silica particles without the addition of SLS showed the lowest surface area, which was only 248.410 m²/g. Increasing the concentration of SLS surfactant on the silica precursor to 3 CMC contributed to an increase in surface area of more than four times to 1,174.225 m²/g. However, after the modification process using aminopropyl, it showed a trend of decreasing the silica particle's surface area. The decrease in the surface area of silica particles after aminopropyl is embedded ranges from 35% to 64% of the initial surface area caused by filling the pore network with aminopropyl ligands.

The morphology of silica particles as a support material also influences the amount of aminopropyl that can be carried. The results show that silica particles synthesized with SLS surfactant have a higher aminopropyl than those without SLS surfactant. The increased surface area, followed by the increasing quantity of macropores in the silica particles as a support material, means that the amount of aminopropyl that can be carried is also higher. Aminopropyl, which was successfully embedded in silica particles with the addition of SLS 3 CMC, had the highest amount, namely 0.9610 mmol/g silica. In contrast, silica particles without SLS addition could only carry around 47%, namely 0.4525 mmol/g silica. The number of amine groups that may be carried is further reduced because, according to SEM pictures, the silica particles developed without macropore structures, causing the active material to just be on the outer surface of the particles. The process of modifying silica particles using the ultrasonic wave-assisted impregnation technique seems to be a quite

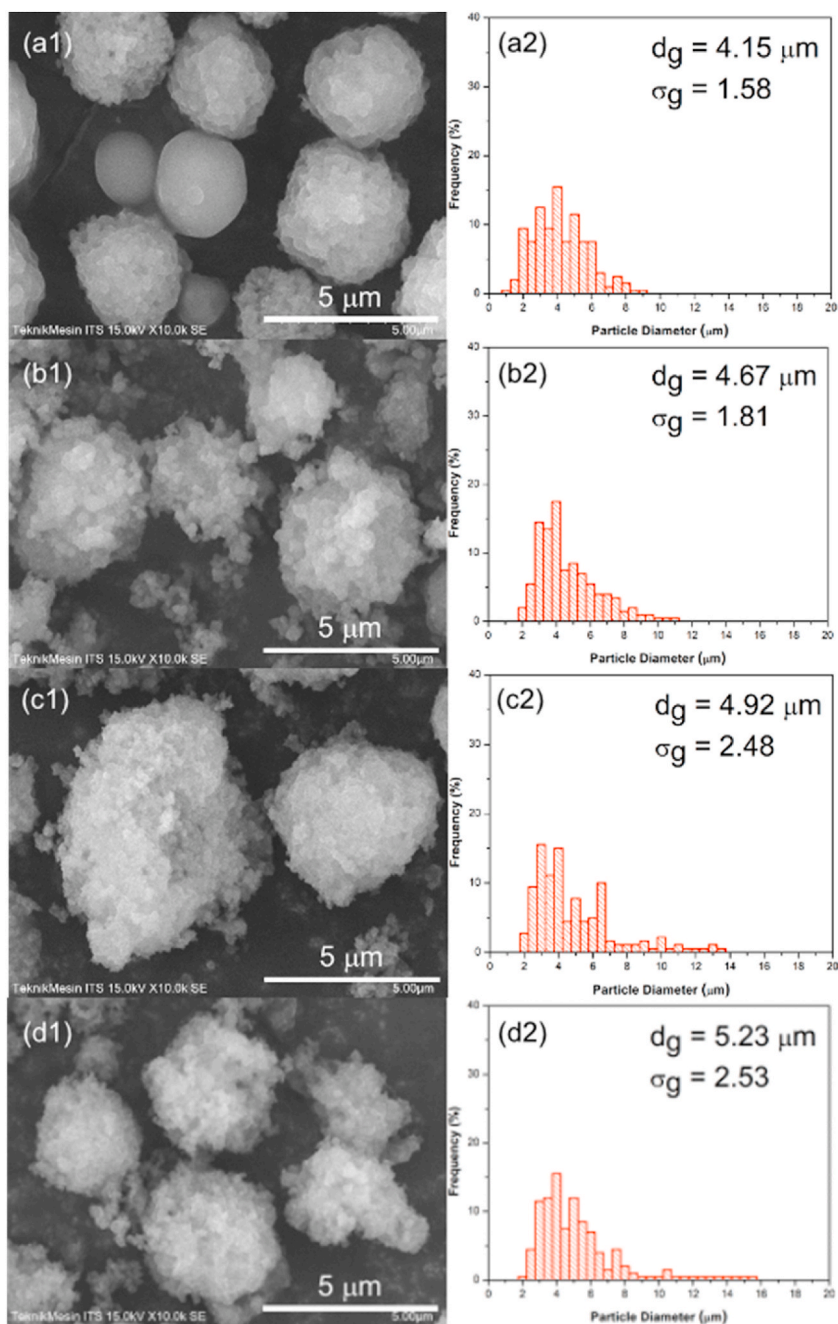


Fig. 7. SEM images and size distribution of amine-modified silica particles without and with the addition of SLS at various concentrations (a1-a2) 0, (b1-b2) 1, (c1-c2) 2, and (d1-d2) 3 CMC.

promising method because when compared to 3 CMC silica particles impregnated conventionally without using ultrasonic waves, they are only able to carry around 51.8% of them when compared to those using the help of ultrasonic waves that are equal to 0.4982 mmol/g silica. The high amount of aminopropyl that can be embedded in silica particles modified by ultrasonic waves indicates that the filling of the pores in the support material can take place better. It may indicate that the ultrasonic waves used during the impregnation process act as a driving force against diffusion resistance due to high pressure in the pores so that the movement of aminopropyl assisted by ultrasonic waves can reach deep into the pores.

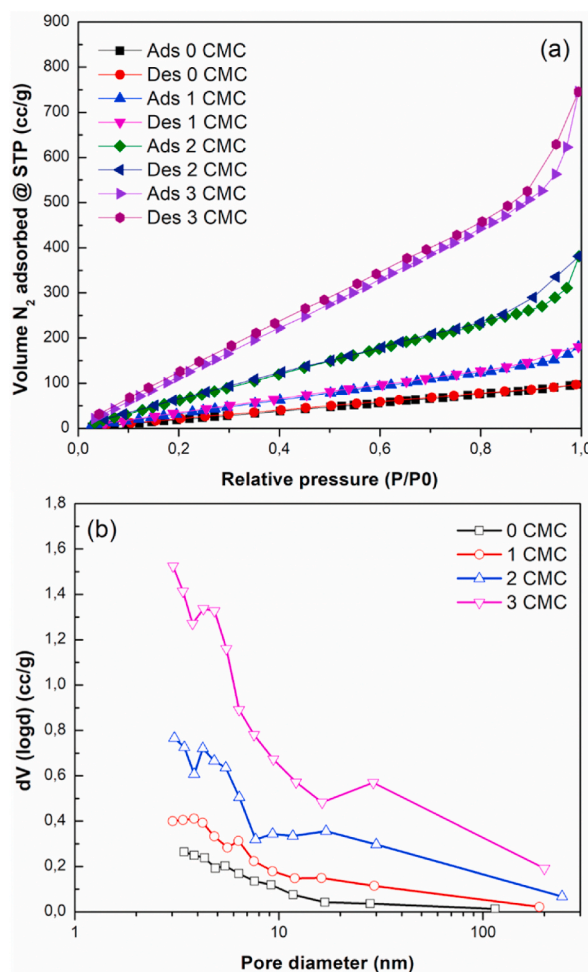


Fig. 8. (a) N₂ adsorption-desorption isotherm and (b) mesopore size distribution of amine-modified silica particles in various SLS concentration via in-situ route.

3.2. Amine-functionalized silica particle characteristics via in-situ modification route

Besides being able to be synthesized through two separate stages of forming and modifying the particle surface, the synthesis of amine-modified silica particles can also be carried out in one step simultaneously. The success of the chemical grafting process of aminopropyl ligands on the surface of silica can be indicated by the appearance of peaks, which can be attributed to the characteristic peaks of the amine and alkane functional groups, as shown in Fig. 6. The distinct peaks of the amine functional groups can be characterized by the appearance of peaks at wave number 1,558 cm⁻¹, which can be attributed to the bond of the primary amine (N–H bend) of the aminopropyl ligand. Aminopropyl bonding to the surface of silica particles can be indicated by the appearance of a peak at wave number 2,930 cm⁻¹, which can be attributed to the stretching of the –CH alkyl group on the CH₂CH₂CH₂NH₂ aminopropyl ligand. The presence of alkane groups on aminopropyl on the silica surface is also confirmed by a peak at wave number 1,476 cm⁻¹. The interaction between aminopropyl ligands and silica can also be indicated by a shift in the characteristic peak of the siloxane group, where the silica particles without aminopropyl modification showed a peak at wave number 1,056 cm⁻¹ and shifted towards a lower wave number to 1,029 cm⁻¹. The silica peaks are also indicated at wave numbers 783 and 693 cm⁻¹, which can be attributed to the vibrational bonds of Si–O and siloxane (Si–O–Si or O–Si–O) functional groups, respectively.

The shape of the amine-modified silica particles created by spray drying appears to be influenced by variations in SLS concentration in the silicate-amine precursor. Fig. 7(a1) shows the morphology of the amine-modified silica particles without the addition of SLS. The resulting particle morphology can be categorized as a particle with a spherical shape that has a relatively smooth surface structure. The morphology of the amine-modified silica particles produced under these conditions follows the ODOP principle and is relatively agglomeration-free. Fig. 7(a2) shows the particle size distribution of amine-modified silica without adding SLS. The resulting particle size distribution has a diameter of less than 10 μm with an average diameter of around 4.15 μm. The particle size distribution pattern shown is uniform, with a standard deviation of 1.58.

A different thing was shown when SLS was added to the silicate-amine precursor, which led to a change in the morphology of the

Table 2
Characteristics of amine-modified silica particles using the in-situ method.

SLS Concentration (CMC)	Average pore size (nm)	Total pore volume (cc/gram)	Specific surface area (m ² /gram)	Amine loading (mmol/gram silica)
0	3.82	0.1503	157.602	1.0123
1	4.40	0.2798	254.185	1.0684
2	4.97	0.5901	475.213	1.1651
3	5.21	1.1540	886.445	1.2845

resulting silica particles. When SLS is added at a concentration of 1 CMC, the resulting particle morphology tends to have an irregular shape with an agglomerated pattern, as shown in Fig. 7(b1). Apart from offering a change in morphology from spherical to irregular shape when SLS surfactant is added to the silicate-amine precursor, changes in the surface structure of the silica particles can also be clearly seen, becoming rougher by forming a hollow network structure like a sponge. The same thing was also found when the SLS concentration was increased to 2 and 3 CMC, as shown in Fig. 7(c1-d1). The morphology of the amine-modified silica particles at higher SLS concentrations did not show significant changes. It was still relatively the same as the particles produced at an SLS concentration of 1 CMC. Changes in the morphology of amine-modified silica particles as a result of increasing the SLS concentration through the in-situ mechanism were followed by an increase in the average particle diameter to be greater from 4.67 μm at an SLS concentration of 1 CMC to 5.23 μm at an SLS concentration of 3 CMC. An increase followed the increase in the average particle diameter in the geometric standard deviation from 1.81 to 2.53. The increase in the standard deviation value for silica particles after adding the SLS template shows that the particle distribution becomes more non-uniform with a wide range of size distribution gaps, as shown by the particle size distribution histogram in Fig. 7(b2-d2).

The formation of agglomerate particles in a spray drying system can occur through two different mechanisms depending on the type of particles that make up it. The first mechanism that facilitates particle agglomeration can be combining several primary particles that follow the ODOP rules. In contrast, the second mechanism combines several primary particles from one droplet and does not follow the ODOP rules. Based on the calculations predicting the particle size of amine-modified silica with adding 1 CMC SLS, a particle diameter of 4.63 μm was obtained. The particle size obtained from theoretical predictions with precursor property parameters and spray drying operating conditions has a lower value when compared with the results of experimental measurements from SEM images, which have a distribution gap range of more than 11 μm . Increasing the concentration of SLS to 2 and 3 CMC showed a tendency to decrease the diameter of the particles produced respectively to 4.38 μm and 3.87 μm . The decrease in particle size demonstrated from the results of theoretical calculations has a difference in value that is not much different even though the SLS concentration has been increased three times. An increase in SLS concentration shows a different trend in changes in particle diameter obtained from theoretical calculation results and experimental measurements. Based on the results of theoretical particle diameter calculations, particle diameter tends to decrease as the SLS concentration increases. In contrast, the results of experimental measurements show an increase in particle diameter when the SLS concentration is increased to 3 CMC. The decrease in particle diameter from the theoretical calculation results could be due to the more dominant influence of SLS on its ability to reduce the surface tension of the precursor without involving the electrostatic and steric influence of SLS as a template. However, the difference in the tendency for changes in particle diameter can be seen that SLS plays a more dominant role as a template for forming meso-macropore structures than its effect on reducing the value of precursor surface tension, which can reduce particle diameter at higher SLS concentrations. Therefore, particle agglomeration shown due to the addition of SLS as a template appears to be formed through a mechanism originating from combining several primary particles following the ODOP rule. Apart from originating from agglomeration by several particles, the particle size of amine-modified silica, which is larger than the results of theoretical calculations, can also indicate the presence of pore structure formation activity on the surface of the particles, which is attributable to the formation of non-ordered porous in the meso-macropore regime.

The increase in surface area by forming a sponge-like hollow network that includes a non-ordered porous structure is also appropriate with the isothermal N₂ adsorption-desorption test, as shown in Fig. 8(a). A porous structure in the isothermal curve profile is indicated by the presence of hysteresis at P/P₀ \geq 0.3 as a particular feature of the type IV curve attributable to the mesoporous characteristics. Hysteresis was found in all variations of SLS concentration, which can be associated with capillary condensation at the mesoporous multilayer stage. An increase in SLS concentration indicates an increase in the amount of N₂ adsorbed at P/P₀ around 0.3, indicating the particles' specific surface area has increased. Amine-modified silica particles without the addition of SLS exhibit mesoporous characteristics, which can be derived from the electrostatic interaction of the nanoparticle's surface charge in the droplet. It shows that the amine-modified silica particles synthesized by the consecutive sol-gel spray drying method have mesoporous characteristics even without adding SLS. Amine-modified silica particles with the addition of SLS seem to experience a dual phenomenon caused by the electrostatic charge of the particles and the steric effect of SLS, causing the surface area of the particles to become higher. The increase in the specific surface area of the particles, along with the increase in SLS concentration, is due to increased pore formation activity by surfactant molecules.

The increase in pore-forming activity due to the steric effect of surfactants, along with increasing SLS concentrations, causes an increase in the mesoporous volume of the particles, as shown in Fig. 8(b). The mesoporous volume increased almost eightfold after adding SLS 3 CMC to 1.100 cc/gram, previously only 0.127 cc/gram. The addition of SLS also increased the volume fraction of the mesoporous particles linearly with the SLS concentration. At a concentration of SLS 1 CMC, the mesoporous volume fraction increased to 94.71% when compared to the particles produced without the addition of SLS, which was only 84.50%. When the SLS concentration was increased to 2 and 3 CMC, the mesoporous volume fraction did not significantly increase and was only around 95%. The increase in

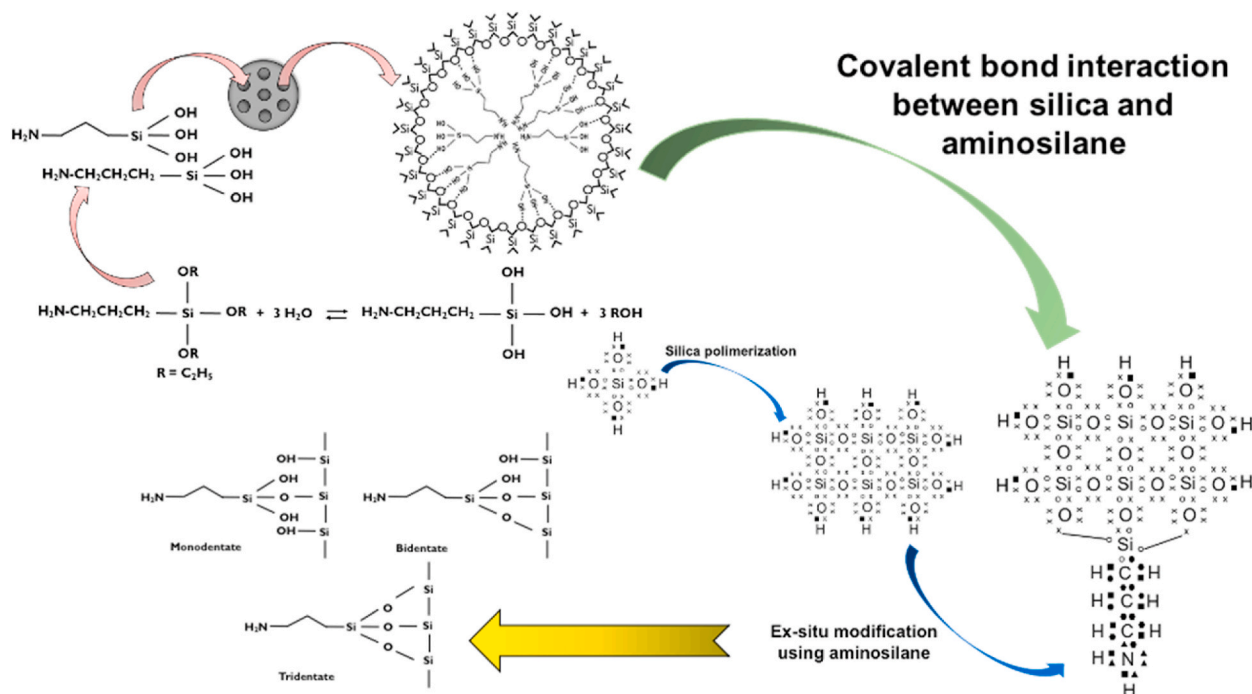


Fig. 9. The surface modification mechanism of silica particles through the ex-situ route.

the mesoporous volume fraction indicates that SLS plays a role in forming mesoporous in addition to those resulting from electrostatic repulsion between nanoparticles in droplets. In addition to increasing the mesoporous volume, adding SLS to the silicate-amine precursors also increases the pore diameter, resulting in a range of pore distribution towards the macropore regime with higher volumes. The macropore regime shown from the BJH distribution can originate from a hollow network, such as a sponge on the particle's surface, as shown by the SEM image.

In addition to showing changes in morphology, adding SLS surfactant to silicate-amine precursors also shows a change in the resulting characteristics, as summarized in Table 2. As indicated by the isothermal N_2 adsorption-desorption profile, the surface area of the particles increases with increasing SLS concentration. The highest specific surface area at SLS 3 CMC concentration reached $886.445 \text{ m}^2/\text{g}$. In contrast, the surface area for amine-modified silica particles without adding SLS was only around 18% , which was $157.602 \text{ m}^2/\text{g}$. The increase in the surface area of the particles is also directly proportional to the amine functional groups that can be grafted onto the surface of the particles. When viewed as a whole, the number of amino acids that can be grafted does not increase significantly, the increase shown is only 21% with the addition of SLS 3 CMC. The relatively constant amine loading indicates that the same ratio of amine modifying agent and silicate precursor results in an even distribution and does not produce a significant difference. This indicates that SLS only contributes to increasing the specific surface area of the particles without causing interference with the grafting distribution of functional groups on the silicate-amine precursor. Compared with the ultrasonic-assisted impregnation method on the ex-situ route, the in-situ method has more aminopropyl which can be grafted onto the surface of silica particles.

3.3. Mechanism of formation of amine-modified silica particles via ex- and in-situ routes

Based on the characteristics of the particles produced through two different mechanical routes, ex- and in-situ, it shows that there are differences in the ability to carry amino groups. Two main factors cause ex-situ modification to have less amine loading than in-situ. Silica particles modified via the ex-situ method involve a condensation reaction between silica and aminopropyl separately, which causes the distribution of amine groups on the surface of the silica particles to be non-uniform. The condensation mechanism of silica particles that occurs first during particle formation causes the number of hydroxyl groups on the surface of the silica particles to decrease and become less reactive after going through the drying process in the spray drying system. In principle, surface modification via ex-situ using porous particles as a support material is by immersing several particles in a modifying agent for a certain time. Another factor that is a challenge in the impregnation process is the high diffusion resistance due to the influence of pressure differences on the surface and inside the particle pores as well as the viscosity of the modifying agent. Therefore, ultrasonic waves are used to reduce the diffusion resistance of the mass transfer modifying agent so that it can penetrate the pores of the silica particles. Aminopropyl will diffuse into the pores and form interactions with hydroxyl on the surface of the silica particles through physical and chemical interactions as shown in Fig. 9. The interaction of hydroxyl groups that occurs between silica particles and aminopropyl influences the stability of the physical bond through van der Waals forces and hydrophobic interactions that are formed to maintain the presence of amino functional groups on the surface of the silica particles so that they do not come off easily.

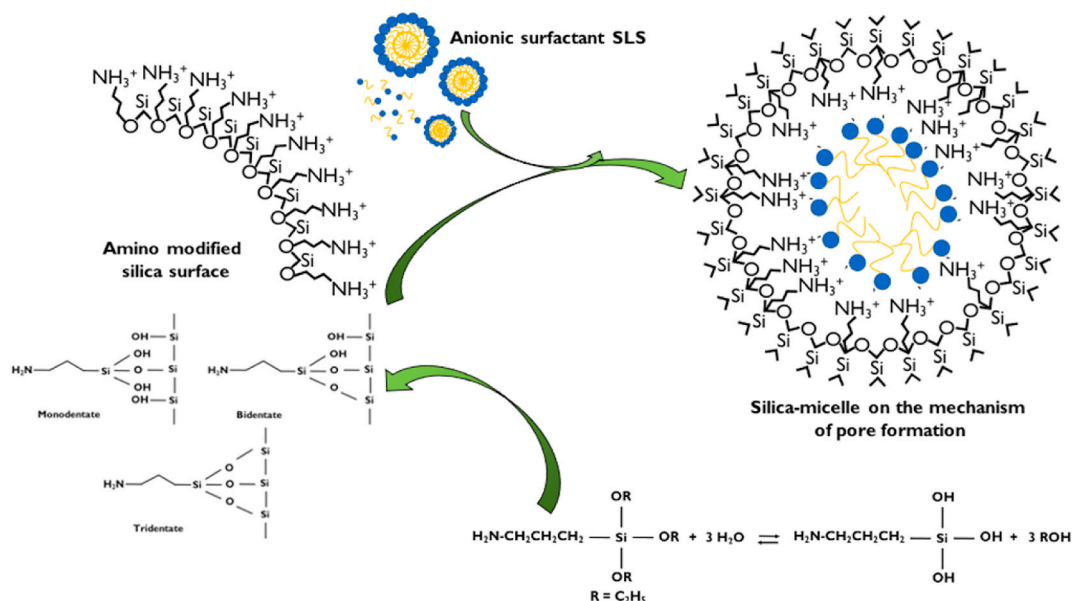


Fig. 10. The surface modification mechanism of silica particles through the in-situ route.

On the other hand, modification of the silica surface with aminopropyl which is only facilitated by physical interactions tends to produce relatively weak bonds compared to bonds produced through chemical reactions. Aminopropyl that does not form strong interactions with the hydroxyl on the silica surface can be released and undergo self-condensation with the surrounding aminopropyl through molecular interactions which causes the quantity of amine loading to decrease. However, surface modification of silica particles using aminopropyl via the ex-situ route also does not rule out the possibility of chemical interactions between free hydroxyl groups and aminopropyl ligands through condensation reactions [13]. The interaction between free hydroxyl and aminopropyl chemically can produce a type of bond that is more stable than physical bonds. One type of chemical bond that can be formed through the interaction of silica with aminopropyl is by forming a covalent bond. The mechanism for forming covalent bonds occurs through the sharing of electron pairs between the O atom in the free hydroxyl group on the silica surface and the Si atom from the aminopropyl which also binds the amine functional group at the other end. Therefore, through these two types of interactions, synergistically, the surface of the silica particles can become more selective towards CO_2 gas molecules.

In contrast to silica surface modification via the ex-situ route, silica particles modified using aminopropyl via the in-situ route involve a simultaneous condensation mechanism between silica and aminopropyl as illustrated in Fig. 10. The condensation reaction that occurs between silica sourced from silicate precursors and aminopropyl can occur in a short time. The interaction mechanism that occurs involves a competitive condensation reaction which can produce bonds between silica monomers and other silica monomers or silica monomers and aminopropyl ligands. The condensation reaction between silica monomers can cause the size of the silica nanoparticles in the colloidal system to grow larger so that they can be precipitated. Therefore, it is necessary to control the concentration of silicate precursors so that the growth of silica nanoparticles in the precursors can be controlled and maintained in a stable colloidal system. Even the distribution of amino functional groups through in-situ condensation reactions can occur because each silica monomer has the opportunity to bind aminopropyl by producing a side reaction in the form of H_2O . This causes the concentration of silicate precursors with the same aminopropyl ratio to produce relatively the same number of amino groups that can be bound. Ideally, three free hydroxyl groups are needed on the surface of a silica particle to theoretically bind one amino group, but other external factors such as treatment during the condensation process also contribute to the ability to bind amino groups. This may be the cause of partial condensation events where only one or two hydroxyl groups can form chemical bonds with the aminopropyl ligand.

Apart from being an active functional group, amino on the surface of silica particles also acts as a co-structure directing agent which functions as an electrostatic charge-matching agent for pore formation with an anionic surfactant template. Silica that has been modified using aminopropyl has a positive surface charge so that it can interact with negatively charged anionic surfactants via the S^--I^+ route where S^- is an anionic surfactant and I^+ is inorganic silica. The surface charge of silica, which was originally negative under alkaline conditions, changes to positive due to the replacement of the hydroxyl functional group with a protonated amine. The amine functional group on the aminopropyl ligand which initially has a neutral charge (NH_2) will generally be protonated under acidic conditions below its isoelectric point ($< \text{pKa}$). In general, the pKa value of amines ranges from pH 9 to 10 depending on the type of amine. Therefore, silicate-amine precursors synthesized at pH 11 will tend to undergo deprotonation. However, the presence of a strong acid such as HCl as a pH-controlling agent in silicate-amine precursors can initiate the formation of positively charged ammonium ions from amines due to accepting protons because more hydrogen ions are available in the environment. The positive charge on the surface of amine-modified silica means that the interaction of anionic surfactants and inorganic silica can be carried out via conventional routes based on electrostatic interactions in alkaline conditions [27,29,30]. Therefore, through this interaction,

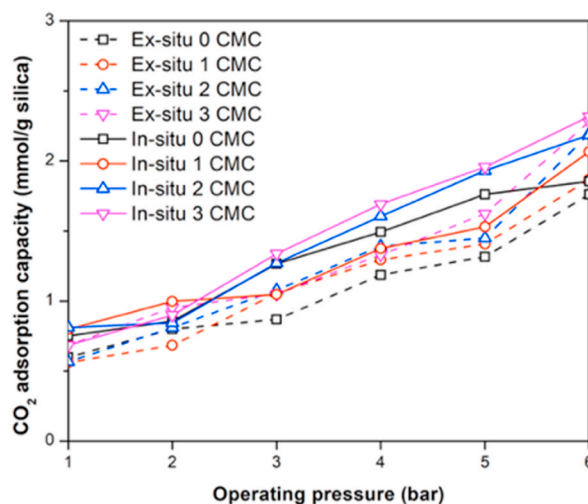


Fig. 11. Comparison of the CO₂ gas absorption capacity of amine-modified silica particles with varying SLS concentrations and modification methods.

anionic surfactants can act as templates to form pore structures on the silica surface with more stable electrostatic interactions.

3.4. Comparison of the amine-modified silica particles' performance via ex- and in-situ routes as carbon capture

Fig. 11 shows the performance of amine-modified silica particles as a selective adsorbent for CO₂ gas. A comparison of adsorbent performance was carried out in the atmospheric pressure range of up to 6 bar to determine the ability to absorb CO₂ gas in different surface modification methods. The ability to absorb CO₂ gas in both types of silica particle surface modification methods along with increasing SLS concentration provides a relatively similar performance quantity profile. The performance of the CO₂ gas adsorbent modified using the ex-situ method shows increased absorption capability along with increasing SLS template concentration ranging from 1.76 mmol/g silica before adding SLS to 2.28 mmol/g silica after adding SLS 3 CMC at operating pressure 6 bars. This shows that the characteristics of the adsorbent, which are represented by high surface area and porosity, can evenly bind CO₂ gas on the surface of the adsorbent. The adsorbent performance shown indicates that increasing the amount of aminopropyl that can be immobilized along with increasing particle characteristics at higher SLS concentrations shows a directly proportional effect on the amount of CO₂ gas that can interact on the particle surface to form charged carbamate. The mechanism of closing part of the pore structure which is attributable to decreasing surface area by aminopropyl has the potential to increase the pressure inside the adsorbent pore and does not appear to have a significant effect because the resulting pore structure is in the macropore regime. Therefore, the pore closure mechanism through the aminopropyl condensation mechanism can be minimized and prevent an increase in pressure in the pore, thus preventing a significant increase in the diffusion resistance for the mass transfer of CO₂ gas molecules into the pore. The same thing was also experienced by the adsorbent modified using the in-situ method, showing an increase in the ability to absorb CO₂ gas along with increasing SLS concentration. The high surface area at an SLS concentration of 3 CMC can increase the ability to absorb CO₂ gas by 24.98% to 2.32 mmol/g silica when compared to the adsorbent without the addition of SLS which is only 1.85 mmol/g silica. Even though the silica adsorbent synthesized with the addition of SLS 3 CMC has relatively the same amount of aminopropyl as the adsorbent without the addition of SLS, in this case, it shows that particle characteristics such as surface area and porosity play an important role in the ability to absorb CO₂ gas in addition to the high amine loading. The even distribution of amines on the silica surface using the in-situ method can increase the ability to absorb CO₂ gas compared to adsorbents modified using the ex-situ method.

4. Conclusion

The surface modification effect of silica particles with APTS via the ex- and in-situ routes on the characteristics of the resulting particles has been successfully investigated using the consecutive sol-gel spray drying method. Surface modification of porous silica particles through the ex-situ route utilizing the principle of ultrasonic wave-assisted impregnation. Porous silica particles synthesized with SLS surfactant templates can produce macroporous structures in a one-step spray drying, which involves forming the particles and removing the template. The increase in particle surface area with increasing SLS concentration shows a linear relationship to amine loading. After modifying the silica particles with the SLS 3 CMC template has the highest surface area around 426.419 m²/g with an amine loading of 0.9610 mmol/g silica. The same thing also happened to the modified silica particles via the in-situ route, where the increase in SLS concentration showed a proportional relationship to the surface area of the resulting particles. In contrast to the ex-situ route, loading amine through the in-situ route at various SLS concentrations showed a relatively constant value. It shows that SLS only acts as a template to increase the surface area without affecting the distribution of aminopropyl. The highest surface area in the in-situ route was also obtained at the SLS 3 CMC template concentration of around 886.445 m²/g with an amine loading of 1.2845 mmol/g

silica. The insignificant difference in amine loading on the in-situ route indicated a more even distribution of aminopropyl due to the simultaneous condensation reaction between silica and APTS. The performance of amine-modified silica particles as a selective adsorbent for CO₂ gas shows a comparable relationship between ex- and in-situ methods on particle characteristics. Adsorbents modified via the ex-situ route show increased CO₂ gas absorption capabilities as the concentration of SLS used to form porous silica as a supporting material increases. The same thing was also shown by the adsorbent modified via the in-situ route showing a comparable relationship between the adsorption ability of CO₂ gas and the surface area of the particles. Amine-modified silica particles obtained the highest adsorption capability via the in-situ route with an SLS 3 CMC template of 2.32 mmol/g silica at an operating pressure of 6 bar.

CRediT authorship contribution statement

Hendrix Abdul Ajiz: Writing – original draft, Formal analysis, Data curation. **W. Widiyastuti:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **Heru Setyawan:** Writing – review & editing, Supervision, Resources. **Tantular Nurtono:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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