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## Effect of Cetyl Trimethyl Ammonium Bromide as Template of Mesoporous Silica MCM-41 from Rice Husk by Sol-Gel Method

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# Effect of Cetyl Trimethyl Ammonium Bromide as Template of Mesoporous Silica MCM-41 from Rice Husk by Sol-Gel Method

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**Abstract.** Rice husk is an agricultural waste that potentially produces high-purity amorphous silica as the source of the precursor of mesoporous silica MCM-41. To obtain pure silica, acid leaching was applied to the rice husk followed by heating treatment in the furnace and synthesized by a sol-gel technique to produce amorphous silica. In this research, mesoporous silica MCM-41 were synthesized by a sol-gel technique assisted by CTAB as a template, then titrated with acetic acid and hydrothermal in the teflon line-autoclave. Various CTAB concentrations were applied as the research variable parameters. X-ray diffraction pattern shows that silica has an amorphous-like curve. FTIR data showed the presence of Si-O-Si function groups in the sample. SEM results showed coral reefs-microstructure with the particle sizes about 243 - 482 nm. TEM image showed the porous structure on the silica surface and formed a hexagonal structure *mcm*-41. The diameter of the shaft was 3.13 - 3.58 nm, hence the resulted silica material is classified as mesoporous material.

**Keywords:** Mesoporous silica, rice husk bio-source, nanoparticle, sol-gel, CTAB

## 1. Introduction

Indonesia is an agricultural country, one of its agricultural products is rice. In the rice production process, one of the natural wastes is rice husks. Conventionally, rice husk has been used as a substitute for wood fuel, growing media, and husk charcoal briquettes. Calcined-rice husk ash has silica content about 86.9-97.3%. The previous study on the rice husk by providing acid treatment [1] and combustion under controlled conditions could produce rice husk ash with high purity of silica content. Also identified other metal impurities such as K, Na, Ca, Mn, Fe, and Mg which affect the purity and color of silica [2].

Silica is generally used in the glass and glass industry as the main ingredient. Nowadays, the silica era began to be developed into mesoporous silica for various applications as biosensors, drug delivery, and other fields that require high material surface area and porous. Mesopore silica can be synthesized by modifying the Stöber process with additional surfactants (for example, Cetyl Trimethyl Ammonium Bromide [CTAB]) [3]. The micelles formed act as a basic framework for the growth of TEOS-based silica. The removal of surfactants will leave the pores in the material. As the number of TEOS is used



to produce mesoporous silica, the production costs will also increase, given that TEOS is not the best commercial source of silica because of high costs, flammability, and handling and storage difficulties. Therefore, using silica as a result of rice husk extraction was chosen instead of TEOS.

Some previous studies reported that synthesizing and characterizing mesoporous silica from rice husks were conducted by calcination method with various temperatures at 800, 850, and 900 °C [4]. Desorption of nitrogen isotherm silica adsorption showed adsorption of Type IV isotherm which is a profile of mesoporous material and the pore size distribution was obtained between 5 to 17 nm. According to such report, the mesoporous silica had been synthesized using heating treatment method. Kumar *et al.* reported that silica aerogel microparticles could be extracted from rice husk ash, continued with water-in-mineral oil emulsion treatment as sol-gel method. Furthermore, Kumar *et al.* reported that surface area was 654 m<sup>2</sup>/g higher than another method for similar materials [5]. Another study reported that mesoporous silica was prepared from bagasse ash as a silica source with PEG-template [6]. Sodium silicate precursor for the mesoporous silica was studied by dissolved silica with NaOH; the variable process was polyethylene glycol (PEG) template. If there was 0% PEG template, pore structure was influenced by pH and ions sodium. Interestingly, PEG increased the surface area significantly up to approximately 656 m<sup>2</sup>g<sup>-1</sup> after PEG removed with solvothermal extraction. Heat treatment at high temperature caused a reducing of pore structure producing a smaller pore diameter, pore volume, and surface area. Such study reported that the pore diameters were mesoporous [7].

In the present study, a simple process has been proposed for mesoporous silica nanoparticles synthesized from a bio-source, such as rice husk ash using CTAB surfactant template. The mesoporous silica nanoparticles were carried out using amorphous silica precursor as a result of extraction of rice husk and surfactant Cetyltrimethyl Ammonium Bromide (CTAB) as a template. The variable parameter of this study was the addition of CTAB concentration as a template to obtain mesoporous silica.

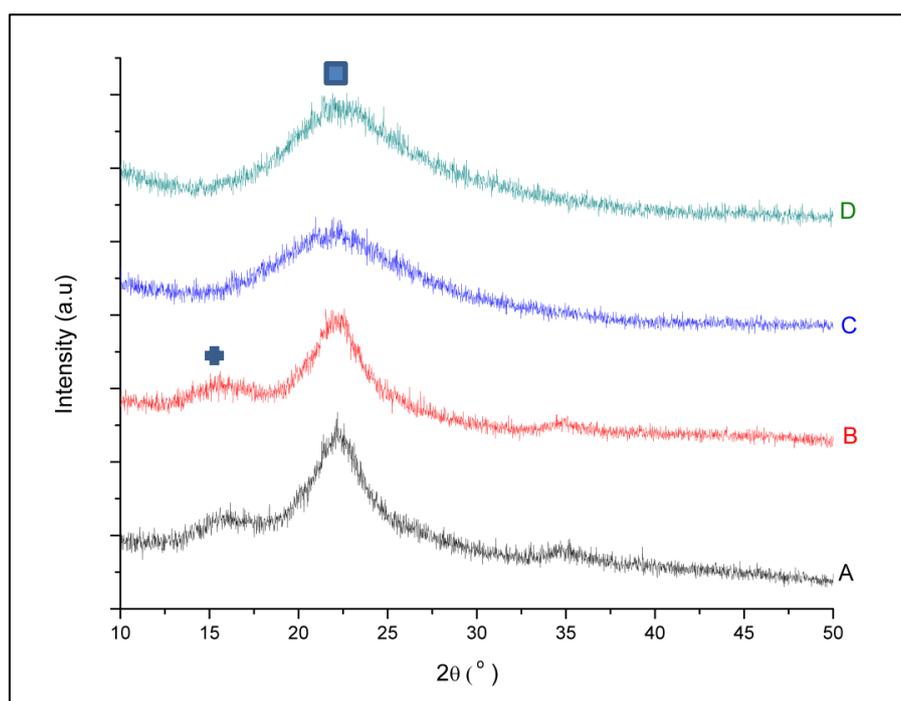
## 2. Methods

Rice husk used from the farmland of Blitar-East Java Indonesia, Cetyl Trimethyl Ammonium Bromide (CTAB) was purchased from HiMedia Laboratories Pvt. Ltd. Sodium hydroxide (NaOH), hydrochloric acid 37% (HCl), Acetic Acid glacial (CH<sub>3</sub>COOH), Methanol 100% (CH<sub>3</sub>OH), 96% Ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and distilled water. First, the rice husk was washed with water and dried. Furthermore, acid leaching treatment was applied to the rice husk and followed by washing it with water to pH = 7. After that, the rice husk was burned in a muffle furnace at 600 °C for 6 hours until getting a white rice husk. The silica extraction process was carried out by dissolving 6 gr RHA into 100 ml of 2M NaOH. It was then filtered to separate the residue from the solution. The filtration solution was titrated with 2M HCl to form a gel; the titration process continued to pH 7. The gel was formed then washed with distilled water to remove salt. To get amorphous silica, the gel was dried for 6 hours at 100 °C.

Mesoporous silica was synthesized using a modified method from the other research method [8]. 6 grams SiO<sub>2</sub> mixed with 100 ml of 2M NaOH, then heated at 80 °C in oil bath for 24 hours to produce sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>). In this study, the variations of CTAB concentration were respectively 1.5%, 1.75%, and 2%. The CTAB was dissolved in 100 ml distilled water according to the ratio of the concentration then stirred for 30 minutes at room temperature. CTAB solution was added to the Na<sub>2</sub>SiO<sub>3</sub> solution slowly under stirring conditions. Stirring for 30 minutes was to make the solution homogeneous. After that, the solution was titrated with 5M CH<sub>3</sub>COOH to pH 10 and stirred for 6 hours at room temperature to obtain a gel, followed by hydrothermal treatment at 100 °C for 24 hours. The gel was aging for 24 hours at pH = 10, filtered and washed using a mixture of distilled water and 96% ethanol, continued with drying at 27 °C for 12 hours. To remove CTAB, it applied reflux process into a mixture of 9 ml of 37% HCl and 160 ml of methanol for 12 hours followed by centrifuge to separate the sediment from the solution. The precipitate was washed with distilled water and dried at 80 °C for 2 hours. The powder was characterized using x-ray diffraction (Pan-Analytical), Fourier transform infrared- FTIR, scanning electron microscope- SEM FEI-INSPECT S50 and transmission electron microscope-TEM, and nitrogen adsorption-desorption isotherms.

### 3. Results and Discussion

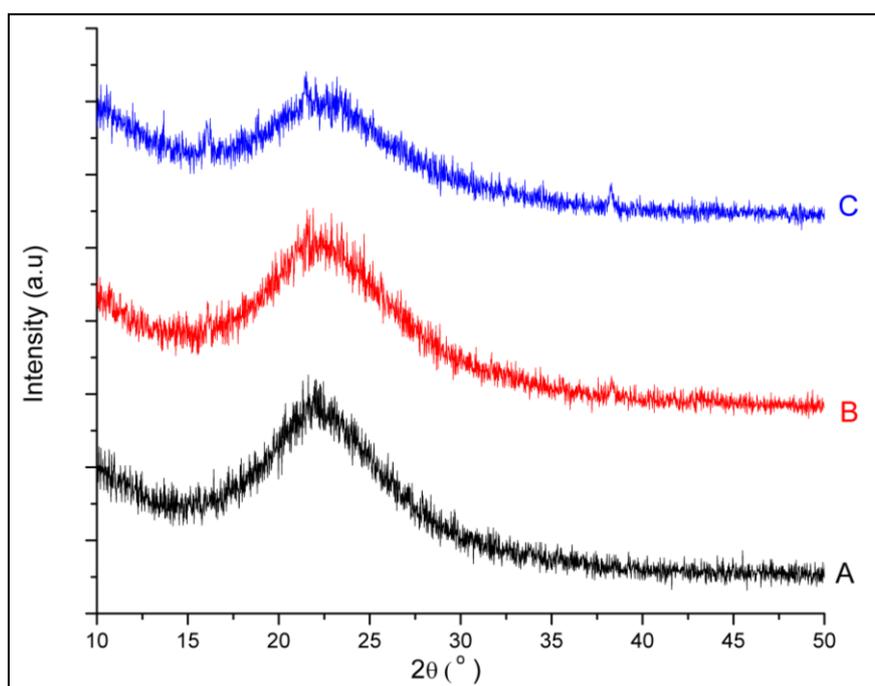
Figure 1 compares the XRD pattern of rice husk (Figure 1.A), rice husk-acid leaching (Figure 1.B), rice husk ash (Figure 1.C), and extracted silica (Figure 1.D). The XRD pattern of rice husk shows peak diffraction at  $2\theta = 16^\circ$ , and  $34^\circ$ , this angle corresponded to the peak diffraction for cellulose ICDD # 00-003-0226 while  $2\theta$  about  $22^\circ$  identified silica phase corresponded to ICDD # 00-001-0424. Chemical treatments such as acid leaching carried out on rice husk can affect cellulose losses. For example, dilute acids have no contributed to the crystal domain but destroy the amorphous region of the fiber [9]. In the diffractogram, there is no significant change on the silica phase, but the cellulose intensity reduces (Figure 1.B).



**Figure 1.** X-ray diffraction pattern of (A) rice husk, (B) leached rice husks, (C) RHA, and (D) extracted silica (■ = silica; + = cellulose)

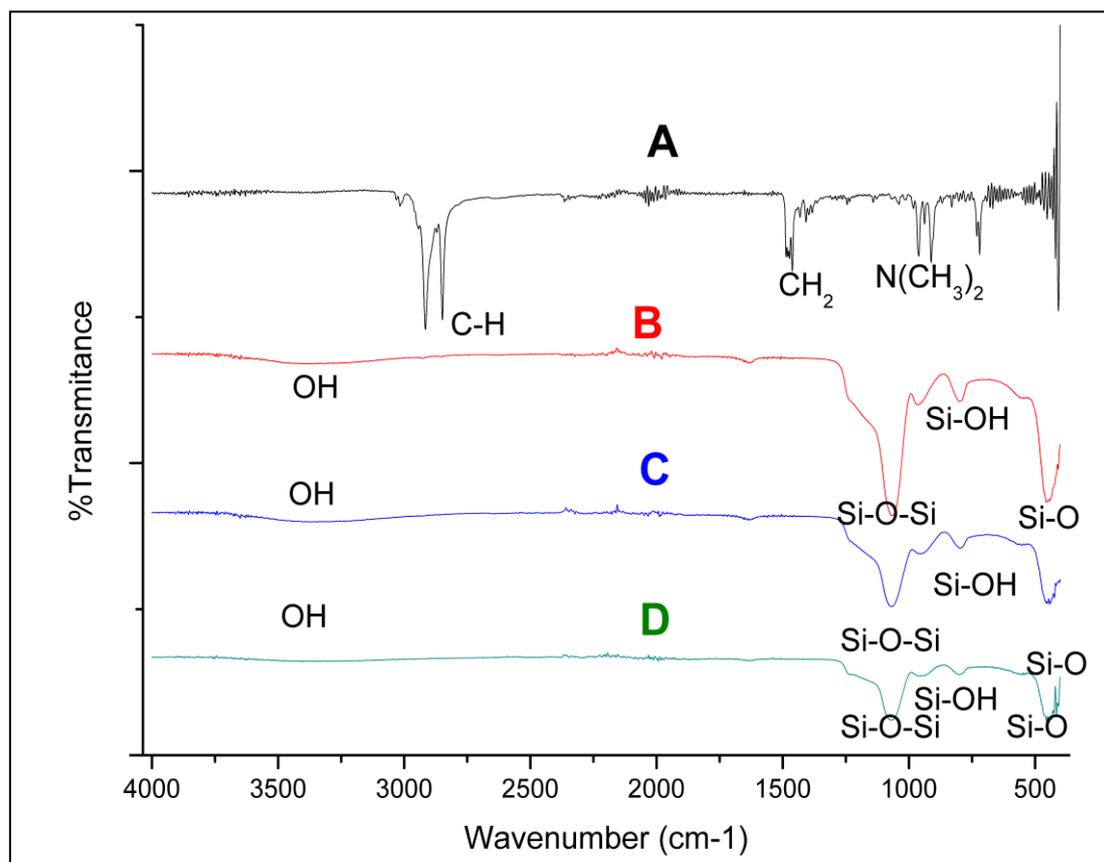
It indicates that the acid leaching can be applied to eliminate cellulose and other organic impurities. Rice husk ash resulted from heating treatment of rice husk. Figure 1.C shows the XRD pattern of rice husk ash that indicates the silica phase. Heating treatment procedure had released all cellulose compounds and other impurities. The XRD pattern shows that at  $2\theta = 22^\circ$  the broadening peak of silica peak diffraction was identified. It is assumed that silica has an amorphous-like structure. The whole chemical process produced silica as shown in Figure 1.D. The XRD pattern shows the silica phase with a narrower peak compared to Figure 1.C. The amorphous-like structure could indicate silica product truly amorphous-phase or silica that has a nano-particle in sized or silica that has a porous structure. It would be proven with the other characterizations (TEM and BET analysis).

X-ray diffraction patterns of 1.5%, 1.7 5%, (C) 2% CTAB surfactant-templated silica have been shown in Figure 2. All various CTAB surfactant-templated silicas had shown an amorphous-phase structure. Increasing CTAB concentration resulted in the wider curve at  $2\theta$  about  $22^\circ$ . Wanyika, *et al.* explained that the wide-angle x-ray diffraction (WAXRD) had amorphous-like pattern that corresponded to the existence of a large porous in the material. The same pattern has been shown in Figure 2; this profile could be assumed that silica has a porous structure [10]. It concludes that the broadening peaks diffraction in the CTAB surfactant-template silica was due to the pores formed in silica.



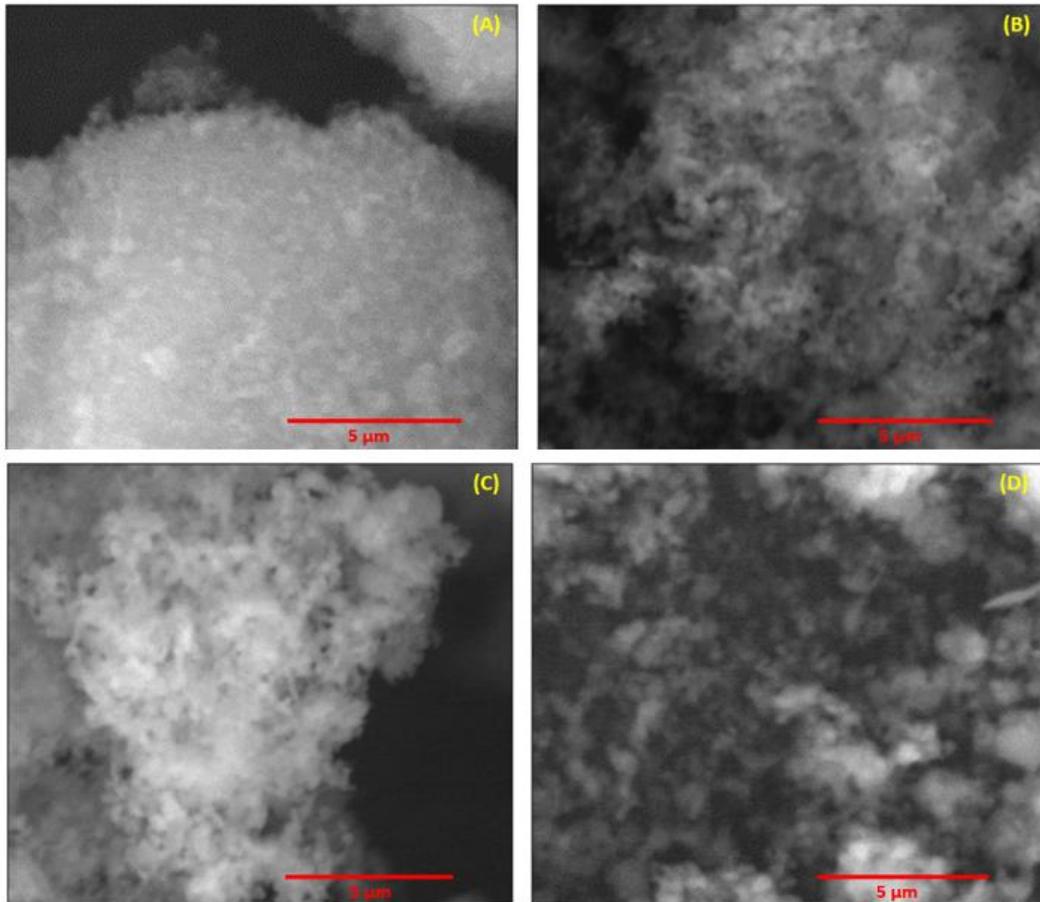
**Figure 2.** X-ray diffraction of silica with CTAB-templated (A) 1.5%, (B) 1.75%, and (C) 2% wt

Figure 3 shows the spectrum of FTIR of pure CTAB (Figure 3.A) and CTAB-templated silica (Figure 3.B-Figure 3.D). FTIR spectrum for CTAB showed a wavenumber =  $418.59\text{ cm}^{-1}$ ,  $718.79\text{ cm}^{-1}$ ,  $730.16\text{ cm}^{-1}$ ,  $911.15\text{ cm}^{-1}$ ,  $960.31\text{ cm}^{-1}$ ,  $1461.89\text{ cm}^{-1}$ ,  $1472.87\text{ cm}^{-1}$ ,  $2848.39\text{ cm}^{-1}$ , and  $2915.75\text{ cm}^{-1}$  that corresponded to the wavenumber of a vibration band of  $-\text{CH}_2-$ ;  $\text{N}(\text{CH}_3)_2$ ;  $-\text{CH}-$  groups which were functional groups of CTAB. Meanwhile, Figure 3.B, Figure 3.C, and Figure 3.D show the FTIR spectrum of 1.5%, 1.75%, and 2% CTAB-templated silica, it showed a wavenumber =  $450\text{ cm}^{-1}$ ,  $790\text{ cm}^{-1}$ ,  $950\text{ cm}^{-1}$ ,  $1070\text{ cm}^{-1}$ ,  $1600\text{ cm}^{-1}$ ,  $2000\text{ cm}^{-1}$ , and  $3400\text{ cm}^{-1}$ . All wavenumber data corresponded to Si-O-Si bond and Si-OH group. Purwaningsih, *et al* reported that FTIR analysis of rice husk, rice husk ash after acid leaching treatment, and extracted silica identified that there were spectra of wavenumber of  $1033.65\text{ cm}^{-1}$  showing the vibration of Si-O-Si. The wavenumber of  $789.54\text{ cm}^{-1}$  showed the symmetrical vibration of Si-O-Si. The wavenumbers of  $548.81\text{ cm}^{-1}$  and  $426.32\text{ cm}^{-1}$  showed the vibration of the Si-O-Si symmetric spurt. There was an H-O-H bending vibration at the wavenumber of  $1637.33\text{ cm}^{-1}$ , and there was a widening band at the wavenumber of  $3338.63\text{ cm}^{-1}$  indicating the Si-OH group [11]. Adding CTAB in extracted silica did not show the wavenumber for the  $-\text{CH}_2-$ ,  $\text{N}(\text{CH}_3)_2$ ,  $-\text{CH}-$  groups. Hence, the reflux acid-methanol process can remove surfactants from silica [8]. Extraction is a mild and efficient method to remove surfactants. Extraction can obtain silicate materials with larger pore sizes in some cases. Other hydroxyl groups can also be kept, enhancing the hydrophilic property and modifying the reactive ability of pore channels. In addition, the resulted sample consisted of wave peaks with the vibration bands of Si-O groups at  $450\text{ cm}^{-1}$ , Si-O-H at  $795\text{ cm}^{-1}$ , Si-O-Si at  $1070\text{ cm}^{-1}$ , and -OH at  $3450\text{ cm}^{-1}$  [12].



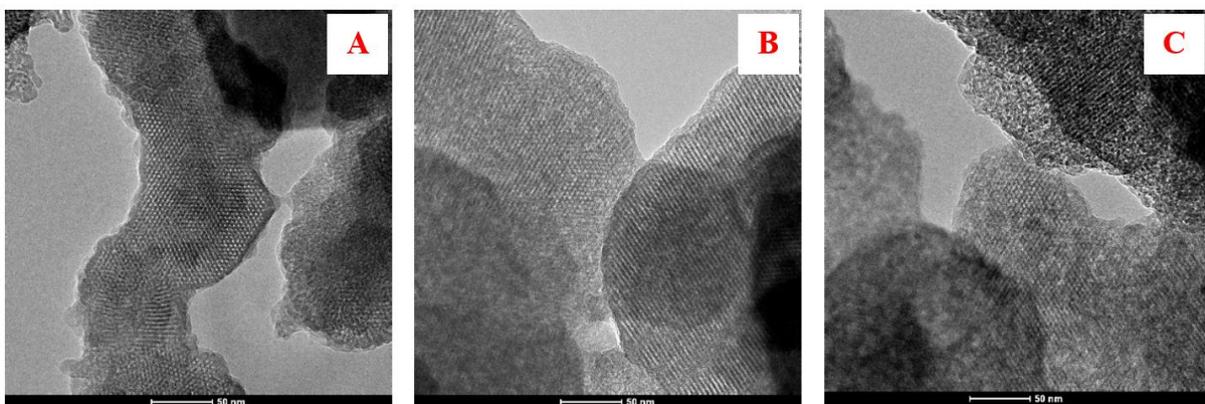
**Figure 3.** Fourier Transform Infra-Red spectrum of (A) CTAB, silica with (B) 1.5% CTAB, (C) 1.75% CTAB, and (D) 2% CTAB

Figure 4 shows a scanning electron microscope of silica-as received (Figure 4.A) and CTAB-template silica (Figure 4.B; Figure 4.C; Figure 4.D). Silica-as have large size particles and a rough surface. Meanwhile, the addition of 1.5%, 1.75%, and 2% CTAB samples (Figure 4. B, C, and D) had particle shape such as coral reef structure, whereas CTAB concentration increased, the silica particle size decreased. The smaller size of silica particles is related to the increase in CTAB concentration. Increasing CTAB concentration causes the formation of more micelle structures so that the bonds that occur between silica and surfactants also increase. Whereas, at a lower silica CTAB concentration which does not bind to the surfactant it binds to the Si-O-Si group which causes the size of the silica to increase. Zhao *et al.* described the mechanism of mesoporous material formation, wherein the part of the  $R_n-N^+(R)_3$  group will bind to silica throughout its surface [12]. Then, silica will form a long chain of Si-O-Si which will become a particle.



**Figure 4.** SEM test results from (A) Silica as-received, (B) 1.5%, (C) 1.75%, and (D) 2% CTAB with a magnification of 20000x

Transmission electron microscope image of 1.5%, 1.75%, and 2% CTAB-template silica samples showed the presence of pores scattered throughout the surface of the silica particles (Figure 5). The pore diameters for 1.5%, 1.75%, 2%CTAB-template silica were 3.12 nm, 3.05 nm, and 2.91 nm respectively. The visible porosity formed a hexagonal arrangement, where the characteristic of MCM-41 was the hexagonal pore arrangement. When TEM image is compared with the results of the study, it has the same results where the porous arrangement is hexagonal or honeycomb-like [13].



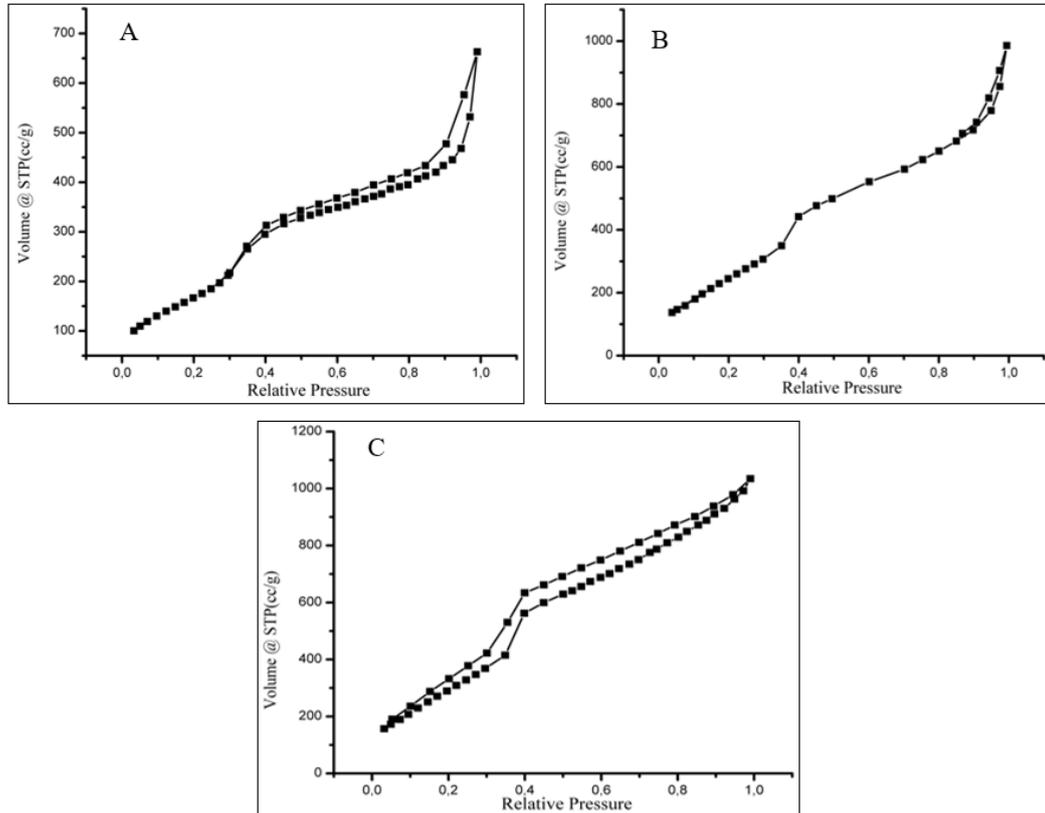
**Figure 5.** HR-TEM test results from silica with the addition of (A) 1.5%, (B) 1.75%, and (C) 2% CTAB

The nitrogen curve adsorption-desorption isotherms of 1.5%, 1.75%, and 2% CTAB-template SiO<sub>2</sub> are shown in Figure 6. According to the five curves of IUPAC standard, the curve adsorption-desorption as shown in Figure 6 has a shape similar to the nitrogen curve of the adsorption-desorption type IV IUPAC isotherms. Type IV curves correspond to the phenomenon of capillary condensation and show a hysterical effect; this is a characteristic of porous solids [14]. This is supported by the results of TEM tests which showed the presence of pore structure on the surface of silica. All CTAB-template silica samples displayed nitrogen sorption isotherms with type IV hysteresis loops characteristic for mesoporous materials.

The data on surface area, average pore size, and total pore volume of silica samples with the addition of 0%, 1.5%, 1.75%, and 2% CTAB are presented in Table 1. It appears that the surface area tends to be wider, for smaller diameter porous sizes. The total pore volume showed a tendency to increase along with the increasing concentration of CTAB; this is consistent with the results of the previous study [15, 16].

**Table 1.** The data on the surface area, average pore size, and total pore volume of silica samples with the addition of 1%, 1.25%, 1.5%, 1.75%, and 2% CTAB

Sample	Surface area (m <sup>2</sup> /g)	Average pore diameter (nm)	Total pore volume (cc/g)
0%	552.429	7.58248	1.047
1.5%	705.501	5.81420	1.025
1.75%	1071.401	5.69372	1.525
2%	1291.436	4.95764	1.601



**Figure 6.** The nitrogen curve of adsorption-desorption isotherms of SiO<sub>2</sub> sample with the addition of (A) 1.5%, (B) 1.75%, and (C) 2% CTAB

#### 4. Conclusion

Our study has successfully synthesized mesoporous silica MCM-41 from rice husk sources using CTAB as a template. It can be concluded that the CTAB concentration effect on the form of mesoporous silica particles size, particle size decreased with the increasing CTAB concentration. Surface area and total pore volume in mesoporous silica increased with the increasing CTAB concentration. Meanwhile, the average size of the porous became smaller. The characteristics of mesoporous silica MCM-41 synthesized had an amorphous-like crystal structure. The mesopore silica synthesized was composed of functional groups Si-O-Si, Si-OH, Si-H, and OH. The mesoporous silica particles formed structures like a coral reef; smallest particle size was 243 nm. Mesoporous silica nanoparticle had formed hexagonal pore arrays. The best composition of CTAB was 2% which had surface area value was 1291.436 m<sup>2</sup>/g; the average pore diameter of about 4.95764 nm and the total pore volume was 1.601 cc/g.

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