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Synthesis and characterization of mesoporous silica nanoparticles (MSNp) MCM 41 from natural waste rice husk

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Abstract. Rice husk contains silica up to 86.9-97.3%, it potentially as precursor silica in the synthesis process of mesoporous silica MCM 41. First, use acid leaching as pre-treatment of rice husk extraction, followed by heat treatment at 600°C in the furnace, continued with sol-gel process to get amorphous silica. Mesoporous silica was synthesizing using CTAB as surfactant to assist porous of silica MCM 41 (CTAB-templated silica). CTAB concentration were 1, 1.25 and 1.5%. Mesoporous silica nanoparticle MCM 41 synthesized by sol-gel method, followed by hydrothermal and reflux methanol + HCl. X-ray diffraction pattern showed that silica has amorphous liked-structure, indicated by peak broadening at 2-theta around 22-24°. Fourier Transformed Infrared-FTIR shown functional group of Si-O, Si-O-H, Si-O-Si, -OH, Si-H, and Si-OH bond have been identified. Scanning electron microscope (SEM) shown particle agglomeration and particle sizes range between 311-482 nm. The desorption adsorption nitrogen analysis (BET analysis) showed that surface area and pore diameter at 1%, 1.25% and 1.5% CTAB have surface area 552.429 m²/g, 768.947 m²/g and 705.501 m²/g. In hence pore diameters are 3.4178 nm, 3.0517 nm and 3.4098 nm respectively.

1. Introduction

The development of mesoporous silica technology has been very developed. Since the discovery of new families of mesoporous molecular sieves such as MCM-41, they have attracted much attention in the filed of catalysis, separation media and host materials for inclusion compounds [1,2]. Many research have been reported, such as various synthesis and formation mechanisms for the M41S family (MCM-41, MCM-48, and MCM-50) [3-16]. These materials serve as an excellent choice for such applications, since they offer high specific surface areas, large and defined pore sizes, defined surface acidity, and excellent mechanical and thermal stability. They are synthesized with surfactant used as template and can be functionalized with different organic groups later. These textural properties should allow fast extraction processes [17-19].

Rice is Indonesia's main agricultural commodity. From paddy to rice, it produces secondary product in the form of rice husks. The use of rice husk itself is still limited to burning brick media. The rice husk ash has a silica content of 86.9-97.3% [20]. Based on previous study, the burning rice husks are expected to replace TEOS as a precursor in the synthesis of MCM 41 mesoporous silica. TEOS is a commercial product that has high prices while rice husks are abundant and inexpensive. Thus, rice husk charcoal is a potential source for producing silica.

Silica that produced from rice husk ash combustion is amorphous silica [21]. Amorphous silica in various conditions is considered more reactive than crystalline silica and has a complicated spherical



structure. This complex structure causes a high surface area, usually above 3 m²/g [22]. The natural specific surface area of silica can still be maximized by using surfactants as templates. Mesoporous silica can be synthesized by modifying the Stöber process with additional surfactants (for example, cetyl trimethyl ammonium bromide-CTAB [23]).

In this paper, we report the synthesis of MCM 41 silica mesoporous from rice husk and its characterization. The detailed phase, crystal structure, porous structure, and their possibility as drug delivery material were explored.

2. Experimental

2.1. Reagents

Rice husk from Blitar, Cetyltrimethyl Ammonium Bromide (CTAB) was purchased from HiMedia Laboratories Pvt. Ltd. hydrochloric acid 37% (HCl), Acetic Acid glacial (CH₃COOH), Sodium hydroxide (NaOH), Methanol 100% (CH₃OH), 96% Ethanol (CH₃CH₂OH) and aquadest.

2.2. Synthesized mesoporous silica MCM 41 from rice husk

Rice husk leached with HCl at 80°C for 2 hours, washed and burned at 600°C for 6 hours to produced rice husk ash (RHA). Dissolved 6 grams of RHA into 100 ml of 2M NaOH and filtered using filter paper. The filtration solution is titrated with 2M HCl until gel formed, the titration process continued to pH 7. Strained the gel using filter paper and dried it at 100°C for 6 hours to produced silica-extracted rice husk. Mixed 6 grams SiO₂ and 100 ml of 2M NaOH and heated at 80°C in oil bath for 24 hours.. Dissolved CTAB 1%, 1.25%, and 1.5% into 100 ml aquades according to the weight ratio and stirred it to produced Na₂SiO₃. Followed by acetic acid titration until pH 10 and stirred for 6 hours. Continued hydrothermal process at 100°C for 24 hours and aging treatment for 24 hours. Then washed using a mixture of distilled water and ethanol. Aging at room temperature for 12 hours. Finally, reflux with solution 9 ml HCl-37% and 160 ml methanol for 12 hours. Separated the sediment using centrifuge and dry it at 80°C for 2 hours.

2.3. Characterization

Fourier transform infra-red (FTIR-Thermo Scientific Nicolet IS10) was employed to determine the chemical bonding, x-ray diffraction (XRD-PanAnalytical X'Pert Pro) was conducted to determine the crystalline structure. Microstructure analysis was observed with microscop electron (SEM-FEI Inspect S50 and TEM). The specific surface area, pore size and pore distribution were determined by Brunauer-Emmett-Teller (BET) Nitrogen adsorption-desorption method using Quantochrome surface analyzer.

3. Result and Discussion

Figure 1 shown FTIR spectrum of pure CTAB and CTAB-templated silica mesoporous. FTIR spectrum of pure CTAB has identified wavenumber at 2915.75 cm⁻¹, 2848.39 cm⁻¹, 1472.87 cm⁻¹, 960.31 cm⁻¹, 911.15 cm⁻¹ and 718.79 cm⁻¹. This peak corresponded to vibrational bands of CH, CH₂, N(CH₃)₂ and CH functional group. According to Becerra (2012), he had reported IR spectra of the surfactants CTAB. The symmetric (ν_s -(CH₂), d₊) and asymmetric (ν_{as} (CH₂), d₋) stretching vibrations of pure CTAB indicate equivalent gauche defects which lie at 2849 and 2918 cm⁻¹. The peaks at 3017 and 1487 cm⁻¹, and at 1473 and 1462 cm⁻¹ were attributed to the asymmetric and symmetric C-H scissoring vibrations of CH₃-N⁺ moieties and to the CH₂ scissoring mode, respectively [25]. FTIR spectrum of CTAB-templated silica various composition 1%, 1.25% and 1.5% had shown wavenumber at 3388.31 cm⁻¹, 1636.71 cm⁻¹, 1070.46 cm⁻¹, 956.95 cm⁻¹, 795.09 cm⁻¹ and 456.15 cm⁻¹. According to the Aldrich handbook library, these wavenumbers indicated functional groups of -OH, Si-O-Si, Si-OH and Si-O. Compared to spectra of pure CTAB, CTAB-templated silica did not show C-H vibrational band and others as showed at pure CTAB spectrum. CTAB-templated silica treatment followed by methanol reflux was able to remove the surfactant template due to the absence of pure CTAB functional groups on the silica reflux results.

Adding CTAB in extracted silica did not show the wave number for the $-\text{CH}_2-$, $\text{N}(\text{CH}_3)_2$, $-\text{CH}-$ groups. Many more surface hydroxyl groups can also be kept, enhancing the hydrophilic property and modifying the reactive ability of pore channels forming.

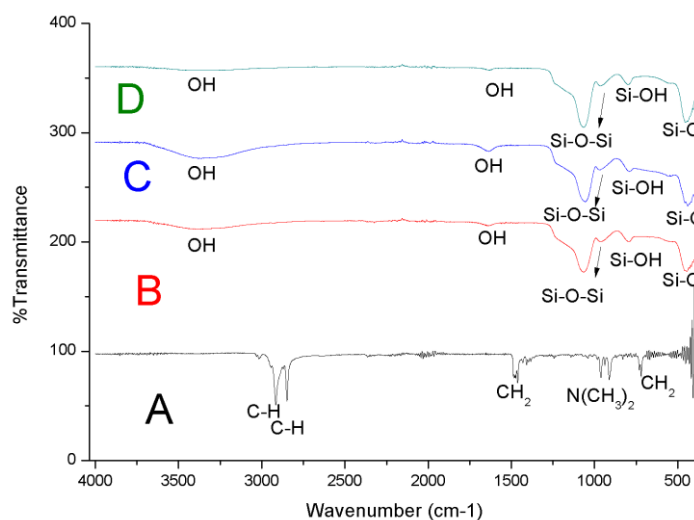


Figure 1. FTIR result of (A) pure CTAB, silica reflux results in concentration (B) 1% CTAB, (C) 1.25% CTAB and (D) 1.5% CTAB.

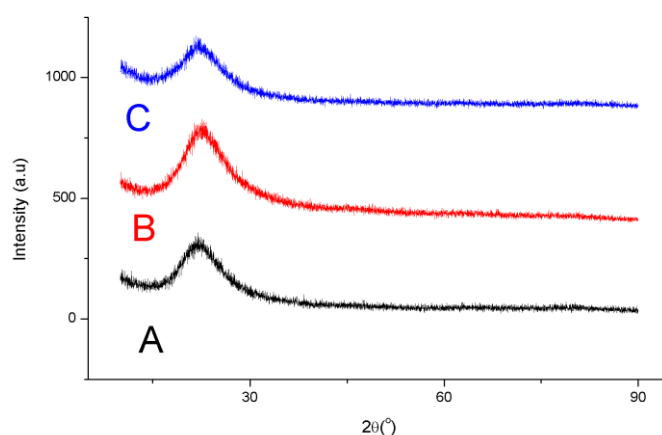


Figure 2. X-Ray diffraction curve of MCM 41 silica mesoporus with surfactant concentration (A) 1% CTAB, (B) 1.25% CTAB and (C) 1.5% CTAB.

Figure 2 shown x-ray diffraction pattern of various CTAB-templated silica for 1% CTAB (figure 2.A), 1.25% CTAB (figure 2.B) and 1.5% CTAB (figure 2.C). XRD pattern of 1% CTAB-templated silica indicated peak diffraction at $2\theta = 22.0155^\circ$. XRD pattern of 1.5% CTAB and 1.5% CTAB-templated silica shown similar curve as 1% CTAB. All XRD pattern correspond to PDF card standard for silica-cristobalite phase ICDD # 00-001-0424. Diffraction patterns showed similarities in profile (figure 2), peaks diffraction broadened at around $2\theta = 22-24^\circ$ as occur in the diffraction pattern of silica amorphous phase.

Amorphous silica is usually present in living things such as diatoms, radiolarians, silicoflagellates, and some sponges. Non-crystalline or amorphous silica has an arrangement of atoms and molecules in

the form of random and irregular patterns [22]. Another study had been reported that peak broadening also indicated porous structure forming. This hypothesis will prove with another characterization measurement such as TEM and BET surface analyzer.

Based on figure 2, the diffraction peaks broadened further as CTAB concentration increases. The sample 1.5% CTAB has the widest diffraction peak compared to other samples. The widening of the sample diffraction peaks indicates the formation of non crystalline structures due to pore formation by the CTAB template. According to Wanyika, et.al (2011) had explained that wide angle x-ray diffraction (WAXRD) have amorphous-like pattern that corresponded to existence of large porous in material. The same pattern had shown in figure 2, this profile could be assumed that silica have porous structure [7]. It concludes that the peak broadening of peaks diffraction in the CTAB surfactant – templated silica is due to the pores formed in silica.

Figure 3 shows scanning electron microscope images of various wt. % CTAB-templated silica, SEM image of 1 % CTAB (A), 1.25% CTAB (B) and 1.5% CTAB (C). Fig 3 shows CTAB-templated silica resulted coral-like structure According to the Figure 3.A, silica particles have the smallest size of 476 nm and the largest is 627 nm, while the average particle size is 482 nm. Figure 3.B shows silica particles have the smallest size of 343 nm and the largest is 542 nm and average particle size is 445 nm. Figure 3.C shows silica particles have the smallest size of 234 nm and the largest is 431 nm, so the average particle size is 311 nm. It was found that the particle size is getting smaller as the concentration of CTAB increases.

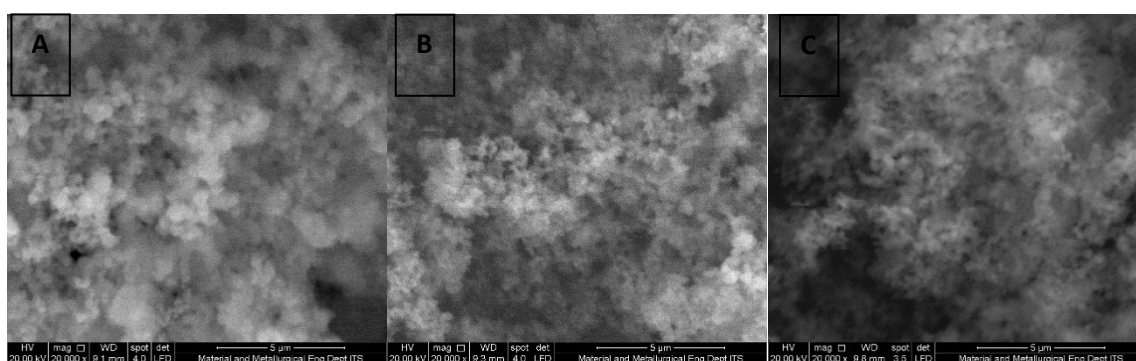


Figure 3. SEM images of silica with (A) 1% CTAB, (B) 1.25% CTAB, and (C) 1.5% CTAB.

Increasing the concentration of CTAB causes the formation of micelle-structures, in hence increasing the bonds between silica and surfactants. Whereas at lower CTAB concentrations, silica that do not bind to surfactants would bind Si-O-Si group itself which causes greater silica particle size. Zhao, et al. (2013) explain the mechanism for the formation of mesoporous material, in which part of the $R_n-N^+(R)_3$ group would bind to silica on the entire surface. Silica formed a long Si-O-Si chain that become a particle [26].

Figure 4 shown TEM images of various concentration CTAB-templated silica, TEM images showed that CTAB induced pores structure in silica particles. Figure 4.A (1% CTAB) shown that silica has a pore diameter 3.58 nm, silica-1.25% has a pore diameter 3.13 nm (B) and silica-1.5% has identified pore size 3.12 nm (C). TEM images also represented pore structure such as honeycomb or hexagonal for all various CTAB, in accordance with the material of the mesoporous silica MCM 41 in other research [24].

Table 1 presented N_2 adsorption-desorption analysis-BET analysis of all various CTAB. It appears that surface area tends to be wider. The total pore volume shows a tendency to increase along with the increasing concentration of CTAB, this is consistent with the results of the study [11] and [12]. An increase in CTAB causes an increasing number of templates so that it can bind more Si-O-H functional groups. When the template removal process is carried out, the number of pores formed increases according to the increase in concentration of the surfactant. Yun-yu, et al. (2012) reported that the increase in CTAB concentration would increase the surface area of the mesoporous silica produced [27].

Table 1 showed that surface area data in this study conformity with Yun-yu et al (2012), because the addition of CTAB concentration has a tendency to increase the surface area of the mesoporous silica produced except at 1.5% CTAB-templated silica. This requires more intensive research to determine the effect of adding CTAB above 1.5%. TEM image and BET surface analyzer for 1.5% CTAB had strongly mentioned that 1.5%CTAB-templated silica had classified as mesoporous material according to pore size ~ 3.12 nm from TEM analysis and 5.814 nm from BET surface analyzer.

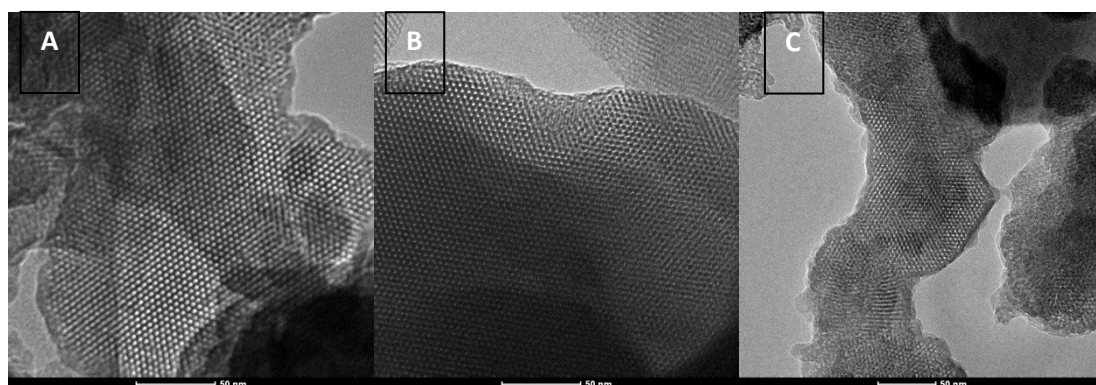


Figure 4. TEM results from silica with concentration (A) 1% CTAB, (B) 1.25% CTAB and (C) 1.5% CTAB.

Table 1. Surface area, average diameter pore size, and total pore volume of silica samples with the addition of 1%, 1.25%, and 1.5% CTAB

No	Sample	Surface Area (m ² /g)	Average diameter pore size(nm)	Total pore volume (cc/g)
1	1%	552.429	7.58248	1.047
2	1.25%	768.947	6.07107	1.167
3	1.5%	705.501	5.81420	1.025

4. Conclusion

MCM 41 silica mesoporus had been successfully extracted from rice husk ash. MCM-41 silica has functional groups -OH, Si-O-Si, Si-OH and Si-O. It has the smallest particle size at a concentration of 1.5% CTAB which is 311 nm with a pore diameter of 3.12 nm and has a honeycomb or hexagonal pore structure. The largest surface area at the greatest concentration of 1.25% CTAB was 768.947 m²/g, the average pore diameter was 6.07107 nm and the pore volume was 1.167 cc/g. CTAB surfactant successfully as pores-templated silica and resulted mesoporous silica nanoparticles.

References

- [1] C T Kresge, M E Leonowics and W J Roth, J C Vartuli, J S Beck 1992 *Nature* **359** 710
- [2] L Mercier and T J Pinnavaia, 1997 *Adv. Mater.* **9** 500
- [3] Kresge C T, Leonowicz M E, Roth W J, Vartuli J C and Beck J S 1992 *Nature* **359** 710
- [4] Beck J S, Vartuli, J C, Roth W J, Leonowicz M E, Kresge C T, Schmitt K T, Chu C T-W, Olson D H, Sheppard E W, McCullen S B, Higgins J B and Schlenker, J L J 1992 *Am. Chem. Soc.* **114** 10834
- [5] Vartuli J C, Schmitt K D, Kresge C T, Roth W J, Leonowicz M E, McCullen S B, Hellring S D, Beck J S, Schlenker J L, Olson D H and Sheppard E W 1994 *Chem. Mater.* **6** 2317
- [6] Vartuli J C, Kresge C T, Leonowicz M E, Chu A S, McCullen S B, Johnson I D and Sheppard E

- W 1994 *Chem. Mater.* **6** 2070
- [7] Beck J S, Vartuli J C, Kennedy G J, Kresge C T, Roth W J and Schramm S E 1994 *Chem. Mater.* **6** 1816
- [8] Huo Q, Margolese D I, Ciesla U, Feng P, Gier T E, Sieger P, Leon R, Petroff P M, Schu"th F and Stucky G D 1994 *Nature* **368** 317
- [9] Huo Q, Margolese D I, Ciesla U, Demuth D G, Feng P, Gier T E, Sieger P, Chmelka B F, Schu"th F and Stucky G D 1994 *Chem. Mater.* **6** 1176
- [10] Tanev P T and Pinnavaia T J 1995 *Science* **267** 865
- [11] Firouzi A, Kumar D, Bull L M, Besier T, Sieger P, Huo Q, Walker S A, Zasadzinski J A, Glinka C, Nicol J, Margolese D, Stucky G D and Chmelka B F 1995 *Science* **267** 1138
- [12] Monnier A, Schu"th F, Huo Q, Kumar D, Margolese D, Maxwell R S, Stucky G D, Krishnamurty M, Petroff P, Firouzi A, Janicke M and Chmelka B F 1993 *Science* **261** 1299
- [13] Stucky G D, Monnier A, Schu"th F, Huo Q, Margolese D, Kumar D, Krishnamurty M, Petroff P, Firouzi A, Janicke M and Chmelka B F 1994 *Mol. Cryst. Liq. Cryst.* **240** 187
- [14] Chen C, Li H and Davis M E 1993 *Micropor. Mater.* **2** 17
- [15] Chen C, Burkett S L, Li H and Davis M E 1993 *Micropor. Mater.* **2** 27
- [16] Cheng C F, Luan Z, Klinowski J 1995 *Langmuir* **11** 2815
- [17] J S Beck, J C Vortuli, W J Roth, M E Leonowicz, C T Kresge, K D Schmitt, C T W Chu, D H Olson, E W Sheppard, S B McCullen, J B Higgins and J L Schlenker 1992 *J. Am. Chem. Soc.* **114** 10834
- [18] S R Hall, C E Fowler, B Lebeow and S Mann 1999 *Chem. Commun.* **201**
- [19] M Algarra, M V Jimenez, E Rodriguez-Castellon, A Jimenez-Lopez and J Jimenez-Jimenez 2005 *Chemosphere* **59** 779
- [20] Y Shiraishi, G Nishimura, T Hirai and I Komasaawa 2002 *Ind. Eng. Chem. Res.* **41** 5065
- [21] Danarto Y C, Nur A, Setiawan D P Kuncoro and N D 2010 *Prosiding Seminar Nasional Teknik Kimia Pengembangan Teknologi Kimia untuk Pengolahan Sumber Daya Alam Indonesia*, Yogyakarta 1-2
- [22] Chandrasekhar S, Pramada P N and Praveen L 2005 *J. Mat. Sci.* **40** 6353-6544
- [23] Kirk R E and Othmer 1984 *Encyclopedia of Chemical Technology 4th Edition* (New York: John Wiley and Sons, Inc.)
- [24] Cai Q, Lin W-Y, Xiao F, Pang W, Chen X and Zou B 1999 *Microporous and Mesoporous Materials* 1-15
- [25] Ghorbani F, Younesi H, Mehraban Z and Celik M S 2013 *J. the Taiwan Institute of Chemical Engineers* 821-828
- [26] Alberto G B, M B Soto, V Soto, J A C, N Casillas, S Prévost, L Noirez, M Gradzielski and José I E 2012 *Nanoscale Research Letters* **7(1)** 83
- [27] Zhao D, Wan Y and Zhou W 2013 *Ordered Mesoporous Materials* (Singapore: Markono Print Media Pte Ltd)
- [28] Yun-yu Z, Xiao-xuan L and Zheng-xing C 2012 *Powder Technology* **226** 239-245