The Effect of Methyl Oleate Variation as a Template in Synthesis of Silica Mesoporous using Tetraethylorthosolocate (TEOS)

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Abstract: Silica material synthesis has been carried out using tetraethylortosilicate (TEOS) as a source of silica, methyl ester oleate as a template, 3-aminopropyltrimethoxysilane as a co-structure directing agent (CSDA), and deionized water as the solvent. The synthesis of silica material was made by varying the mass of methyl ester oleate, namely 3.7358 g, 4.2695 g, 4.8032 g, 5.3369 g, and 5.8706 g. The TEOS and APMS mixture was added to a mixture of methyl ester oleate, 0.1 M HCl, and deionized water and then stirred at room temperature for 2 hours. The mixture was then cooked in an oven at 80º C for 72 hours. Separation of the product is done by centrifugation, The resulting solid is dried and then calcined at 550º C for 6 hours. The XRD analysis results of the product showed diffraction peaks which widened at 12º to 30 º which indicated that the resulting material was amorphous. The FT-IR spectrum shows the presence of Si-OH and Si-O-Si groups which are characteristic of silica material. SEM analysis shows the existence of hollow particles with non-uniform size. Nitrogen isotherm (BET) adsorption shows type IV isotherm curves and H1 type hysteresis loops with uniform pore sizes on the variation of methyl oleate 4.8032 g, which is 2.28 nm. This identified that the optimum conditions for the synthesis of silica mesoporous material with the methyl ester oleate template had been achieved.

1 INTRODUCTION

Porous material according to IUPAC can be classified into three categories based on pore diameter, namely: (i) micropore (d <2 nm), (ii) mesoporous (2 nm <d <50 nm), (iii) macropore (d> 50 nm) , and (iv) megapories (> 7500 nm). The development of the synthesis, characterization, and application of porous materials has long been carried out due to its wide use in adsorption, drug delivery, separation, catalysts, and sensors. Modifications to the synthesis of porous materials are still being carried out for the development of material structures such as porosity and pore diameter.

Silica mesoporous material can be synthesized by adding templates in the form of anionic, cationic, or non-ionic surfactants, or non-surfactant tempalates, where the surfactant charge is based on the head group load. Pore diameter can be controlled by changing the molecular carbon chain length of the template. Templates are used as molds (auxiliaries and guides) in the formation of pores, where primary colloidal particles will fill the gaps between the template arrangements, so that when the

template is removed from silica particles a hollow particle is formed. Templates can form pores due to the presence of micelles from the surfactant. Silicate precursors are formed around the surfactant micelles by the crystallization process and then form amorphous silica polymers that surround the micelles. The micelles are then removed by calcination, thus leaving a cavity which is then referred to as a pore.

Research on synthetic silica material using anionic surfactant templates is undergoing development. (Yokoi et al., 2006) Synthesized silica material using sodium laurate and 3-aminopropyltriethoxysilane (APS) co-structure directing agent (CSDA). The results show that with the increase in APS mass used, the pore diameter decreases from 4.0 nm to 3.3 nm. (Han et al., 2011) Synthesize mesoporous silica with oleic acid tempalte with the addition of ethanol as a solvent. The results show that the more ethanol used, the pore diameter decreases regularly. (Wan & Zhao, 2007) Synthesized silica mesoporous material using sodium n-lauroylsarcosin (Sar-Na) with variations in HCl mass. The results show that the decrease in pH

causes an increase in pore size from 3.1 nm to 3.3 nm. (Tsai et al., 2011) Synthesized mesoporous silica nanoparticles (MSNs) with ethylene glycol phosphate monoester surfactants (PMES) with variations of 3-aminopropyltrimethoxysilane (APTMS). The results show that with increasing APTMS ratio, pore diameter will increase and decrease regularly. (Andriayani et al., 2018) synthesized silica material with sodium ricinoleate with 0.1M HCl variation producing a pore size of 2.2-3.8 nm, and examined the effect of variations in HCl concentrations in the synthesis of mesoporous silica materials using methyl ester ricinoleate as a template (Andriayani et al., 2018). Although research on the synthesis of mesoporous materials with anionic surfactant templates continues to develop, reports of the use of methyl oleate as templates have not been conducted so far, so that optimum conditions for obtaining silica mesoporous materials with good porosity and have a uniform pore distribution.

Methyl oleate is clear yellow and has nineteen carbon chains, an ester of oleic acid. Synthesized through the reaction of esterification with methanol and catalyst, both acid catalyst or base catalyst. (Ahn et al., 2012) Synthesized graphene in which methyl oleate epoxy from methyl oleate to form oleo-graphene oxide (oleo-GO) which can dissolve in water, thus forming nanocomposite graphene. (Bao et al., 2017) esterified oleic acid to methyl oleate using $Zr\text{-}SO_3H$ @ CMC catalyst which was used as biofuel.

Based on the above explanation, researchers are interested in developing research on synthetic silica mesoporous materials with variations in the number of methyl oleate templates. The number of templates plays a role in determining the characteristics of silica mesoporous material. A high amount of surfactant will increase the formation of micelles, so that it will produce more pores. However, if the amount of surfactant is excessive, it will produce more micelles and large pores and cause the formed silica matrix to become brittle (easily broken), so that optimum conditions will be sought.

2 MATERIALS AND METHODS

2.1 Materials

The materials used in this study include : Oleic Acid, tetraetilorthosilicat (TEOS), 3-aminopropiltrimetoksisilan (APMS), HCl 0.1 M, Deionized Water, n-hexane, Calcium Chloride($CaCl_2$), methanol, Methyl Oleate, sulfuric acid (H_2SO_4).

2.2 Methods

Esterification of Oleic Acid

In a three neck flask (250 ml), oleic acid (40 g ; 0.134 mol), dried methanol (85.76 g; 2.68 mol), and $H_2SO_{4(p)}$ (0.8 g) catalyst, then heated in reflux circuit at a temperature of 60-70°C while stirring for 3-4 hours. The reaction results obtained added aquadest. After that the methyl ester formed is extracted with n-hexane. Oleic oil methyl esters obtained were analyzed using GC-MS.

Synthesis of Mesoporous Silica

Into the beaker glass, 3.7358 g of methyl ester oleate (0.01126 mol) are added, then add 100 ml of demineralized water and stir for 20 minutes. Then add 30 ml of 0.1 M HCl while stirring at room temperature for 5 minutes. Then a mixture of 3.74 g TEOS (0.018 mol) and 1 g APMS (0.00559 mol) was made and stirred for 5 minutes in a closed condition. The TEOS and APMS mixture was added to the mixture of methyl ester oleate, demineralized water, and HCl and then stirred for 2 hours. Then aging in an oven at 80°C for 72 hours. The product is separated using a centrifugator and washed with demineralized water and then dried. The resulting solid was calcined at 550°C for 6 hours. The results obtained were characterized by FT-IR, XRD, SEM and BET analysis.

Table 1: Condition reaction of synthesis mesoporous silica.

Treatment	TEOS (mol)	Methyl Oleate (mol)	Methyl Oleate (gram)	APMS (mol)	HCl (ml)	Stirrer Time (hours)
Run-1	0.018	0.00126	3.7358	0.00559	30	2
Run-2	0.018	0.0144	4.2695	0.00559	30	2
Run-3	0.018	0.0164	4.8032	0.00559	30	2
Run-4	0.018	0.0180	5.3369	0.00559	30	2
Run-5	0.018	0.0198	5.8706	0.00559	30	2

3 RESULTS AND DISCUSSION

3.1 GC-MS Analysis of Methyl Oleate

The esterification results of oleic acid were analyzed using GC-MS to see the purity of the methyl oleate produced. The results of the GCMS analysis showed that the percentage of methyl oleate was the largest at 86.77%.

3.2 Synthesis of Mesoporous Silica

Into the beaker glass, methyl ester oleate is added with demineralized water. Then added 0.1 M HCl then stirred at room temperature for 1 hour. The mixture of terraethylortosilicate (TEOS) and 3-aminopropyltrimethoxysilane (APMS) was stirred for 5 minutes, then the mixture of terraethylortosilicate (TEOS) and 3-aminopropyltrimethoxysilene (APMS) was added to the beaker glass containing a mixture of methyl ester oleate, HCl, and water in the demineralized water room temperature for 2 hours. Aging was carried out in the oven at 80°C for 72 hours. The product is separated by centrifugation and then dried and then calcined at 550°C for 6 hours. The result was 0.7873 g, 0.7932 g, 1.0904 g, 0.8576 g, and 0.8963 g.

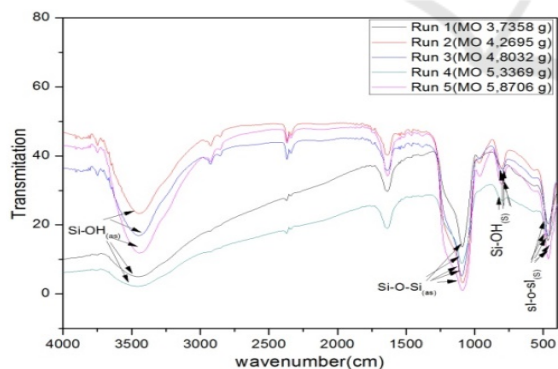### 3.3 FT-IR Analysis of Material Mesoporous Silica

Figure 1: FT-IR analysis of mesoporous silica.

The picture above shows that the methyl ester oleate used as a template was lost during calcination. This can be seen from the absence of $C = O$ uptake in the range 1725 cm^{-1} and $C = C$ uptake in the range 1680-1640 cm^{-1}. It can also be seen from the figure above that all mesoporous materials with the addition of various oleic methyl esters show the absorption peak between 3448.72 cm^{-1} (broad) given by the OH group strain (v_{as} Si-OH), whereas at 802.39 and 794.67 cm^{-1} is caused by the presence of Si-OH symmetrical groups (v_s Si-OH). Other absorption peaks were seen at 1095.57 and 1087.85 cm^{-1} (strong) given by the strain Si-O-Si (v_{as} Si-O-Si), while at 462.92-455.20 cm^{-1} caused by the symmetric group Si-O-Si (v_s Si-O-Si).
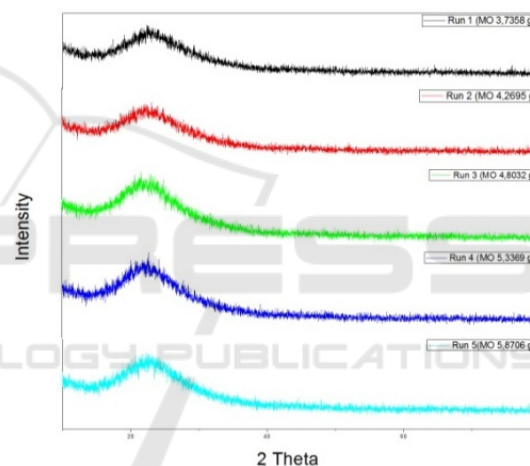
3.4 Difraction of XRD Mesoporous Silica

Figure 2: Difractogram for mesoporous silica.

Table 2: Functional group of mesoporous silica.

Silica Material	Functional Group Wavelength			
	Si-OH$_{(as)}$	Si-O-Si$_{(as)}$	Si-OH$_{(s)}$	Si-O-Si$_{(s)}$
Run-1(MO 3.7358 g)	3448.72	794.67	1087.85	462.92
Run-2(MO 4.2695 g)	3448.72	802.39	1085.85	462.92
Run-3(MO 4.8032 g)	2448.72	802.39	1095.57	462.92
Run-4(MO 5.3369 g)	3448.72	794.67	1095.57	470.63
Run-5(MO 5.8706 g)	3441.01	802.39	1087.85	462.92

From the picture above can be seen XRD diffractogram at an angle of 2θ which widens between 120º to 38º. Diffraction peaks that widen from silica material in run-1, run-2, run-3, run-4, and run-5 are 22.32, 23.07, 21.66, 22.61, and 22.28 which shows that the material produced is silica and has an amorphous structure. This is consistent with the data found in the literature (Andriayani et al., 2013; Zhao et al., 2014).
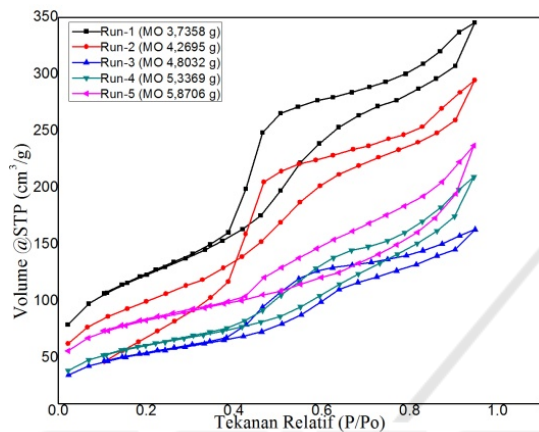
3.5 Isoterm Adsorbsi-desorbtion

Figure 3: Isoterm adsrobtion-desorbtion of mesoporous silica.

Graphs of run-1, run-2, run-3, run-4, and run-5 silica material isotherm silica material show loop hysteresis at relative pressure (P/P_o) between 0.45-1 and physisorption isotherm type IV according to the IUPAC classification (Gregg & Sing, 1982). The hysteresis loop shape in run-1, run-2, and run-3 silica material is H1 type which shows that porous material is cylindrical, such as pore ducts or agglomerates of solids with coarse homogeneous fields (Roque-Malherbe, 2007). Whereas run-4 and run-5 has hysteresis loops of type H3, namely the existence of nonrigid aggregates of particles such as plates which have pore-shaped gaps.

Pore size distribution of the resulting silica material can be seen in the following figure:
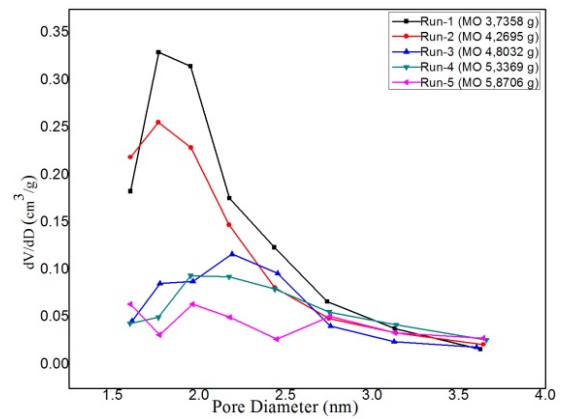

Figure 4: Pore size distribution for mesopoorous silica.

In Figure 3.4, several different peaks of each of the silica material produced indicate that the pores formed are not uniform. The resulting pore diameter starts from 1.59 nm - 3.65 nm, so it can be classified into micropore and mesoporous sizes. The dominant pore size for variations in the addition of methyl ester oleate to run-1, run-2, run-3, run-4, and run-5 are 1.77 nm, 1.77 nm, 2.18 nm and 2.45 nm, 1.96 nm, and 2.00 nm and 2.769 nm.

3.6 Microskop Electron Scanning (SEM)

Based on the BET test, it was found that run-3 silica material has an even distribution of pore size, so to find out the morphology of run-3 silica material is done with SEM photographs with various magnifications of 5,000 and 20,000 times. The SEM photo is shown in the image below:
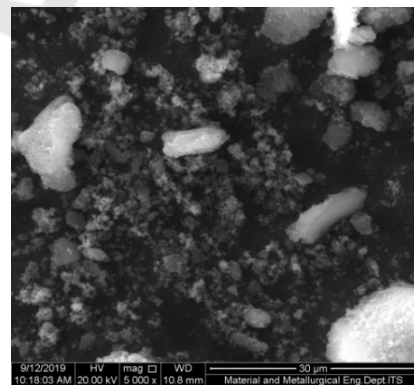

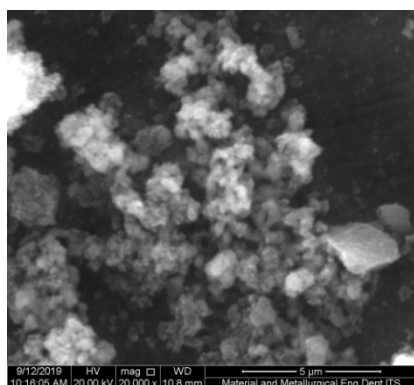Figure 5(A): Magnification 5,000 times.

Figure 5(B): Magnification 20,000 times.

SEM photos in Figure (A) with a magnification of 5,000 times, it appears that the shape of the particle is not clear and only looks uneven chunks and there are small aggregates that are dispersed on the surface of the material, while at magnification 20,000 times (figure B) have started to clearly see diverse particle shapes, such as large lumps and spherical shapes. And inside the particle there is a gap.

4 CONCLUSIONS

The characteristics of the mesoporous silica material produced, namely the FT-IR spectrum shows the presence of silanol groups (Si-OH) and siloxane groups (Si-O-Si) which are characteristic of silica material. XRD diffractogram shows the diffraction peaks widened at angle of 2θ between $20\text{-}40^{\circ}$, so that the silica material formed is silica mesoporous. SEM photos show the dispersed aggregates on the surface of the material in a non-uniform pore size condition. The isotherm nitrogen adsorption descent with the BET method shows a type IV isotherm curve that is an isotherm type for mesoporous material and has H1 hysteresis loop type in run-1, run-2, and run 3 silica material. While run-4 and run- silica material 5 has hysteresis loop type H3. The dominant pore diameter sizes are 1.77 nm, 1.77 nm, 2.18 nm and 2.45 nm, 1.96 nm, and 2.00 nm and 2.769 nm, respectively.

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