The effect concentration of tetraethylorthosilicate and variation HCl 0.1M for synthesis mesoporous silica using oleic acid as template and 3-aminopropyltrimethoxysilane as co-structure directing Agent

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Abstract. Synthesis mesoporous silica using oleic acid as template and 3-aminopropyltrimethoxysilane as co-structure directing agent has been conducted. As a silica source used tetraethylorthosilicate. The reaction was carried out under three conditions: first, reducing the concentration of tetraethylortosilicate and 3-aminopropyltrimethoxysilane and varying the volume of HCl 0.1M; second, increasing the concentration of tetraethylortosilicate and 3-aminopropyltrimethoxysilane by varying the addition of HCl 0.1M and the third was carried out with the addition of methanol but without the addition of HCl 0.1M. The obtained silica mesopores were characterized by infrared spectrometer, X-ray diffraction and adsorption-desorption isotherm and scanning electron microscopy.

1. Introduction
The porosity of a material affects the physical properties of materials such as density, heat conductivity, strength and so on. The size of pore diameter (d) according to IUPAC is classified into 3 (three) types: (i) micropore (d < 2 nm), (ii) mesoporous (2 nm < d <50 nm) and (iii) macropore (d > 50 nm) [1, 2].

The synthesis of mesoporous material is growing rapidly to date because it has unique properties such as a more regular pore structure, large surface area and a more uniform pore size distribution. It can be applied as a catalyst [3, 4], adsorbent [5], drug delivery [6, 7], biosensor [8], optics [9] and others.

The interaction of inorganic materials with organic components (templates) such as surfactants greatly influences the porosity characteristics. In this case, silica interaction with templates can be assisted using 3-aminopropyltrimethoxysilane (APMS) compounds that act as co-structure directing agent (CSDA). In the APMS molecule the alkoxylene group will condense with the silica and the ammonium group will interact electrostatically with the anionic surfactant (interaction of S N+I- (S- = anionic surfactant, N+ = CSDA and I- = silica) [10].

The use of anionic surfactants in the synthesis of mesoporous materials is still poorly reported, due to the difficulty of obtaining the right conditions to obtain a high degree of pore regularity. We have synthesized mesoporous silica material from tetraethylortosilicate (TEOS) using sodium ricinoleic
acid as template and 3-aminopropyltrimethoxy silane (APMS) as co-structure directing agent (CSDA) by varying addition of HCl 0.1 M [11]. In this paper, we will report the synthesis of silica mesoporous material using oleic acid as a template. Oleic acid is the largest component in palm oil which is one of the abundant plantation products in Indonesia, especially North Sumatera. The application oleic acid such as: the influence of oleic acid on induction of steatosis and cytotoxicity in mouse liver cells [12], modification of surface silicate mesoporous [13] and effect of oleic acid on crystallinity of mesoporous calcium carbonate [14].

2. Research and method

2.1. Materials
Tetraethylorthosilicate (TEOS, 98%) and 3-aminopropyltrimethoxy silane (APMS) were purchased from Sigma Aldrich, oleic acid purchased from Merck, hydrochloric acid from Malincrot and deionized water obtained from PT Sumber Aneka Karya Abadi.

2.2. Characterizations
Characterization functional group of material silica by fourier transform infrared (FT-IR) instrument conducted at Pusat Penelitian Kimia laboratory, LIPI Jakarta Indonesia. The X-ray diffraction (XRD) pattern were obtained on a Philip PW 1710 diffractometer with CuKα radiation at 25 kV and 17 mA conducted in UNY Yogyakarta, Indonesia. Nitrogen adsorption/desorption isotherm were measured at 77.30K using a Quantachrome Instruments Quantachrome Autosorb Automated Gas Sorption System Report and outgas at 150.0°C. The pore size distribution (PSD) was calculated by the BJH (Barett-Joyner-Halenda) method, conducted in BATAN Indonesia. Morphology product silica characterized by SEM-EDS Carl Zeiss-Bruker EVO MA10 and conducted in Laboratory MABES POLRI Indonesia.

2.3. Synthesis of Silica Mesoporous Material Using Oleic Acid as Template (Reduction of TEOS Concentration and Variation of Volume HCl 0.1M).
Into beaker glass incorporated oleic acid and added aquabides while stirring. Then add HCl 0.1 M and stirred for 1 hour (mixture A). Into another beaker glass a mixture of B is made up of tetraethylorthosilicate (TEOS) and 3-aminopropyltrimethoxy silane (APMS) and stirred for 5 minutes. The mixture B and mixture A were mixed and stirred for 2 hours. Furthermore, it is aged in the oven at 80 °C for 4 days until a perfect solid is formed. After the maturation process silica solids are separated and washed with aquabides and dried at 50°C. The product silica were calcined in a furnace at 900°C for 4 hours. Synthesis of mesoporous silica was variated by varying the volume of HCl 0.1 M, as seen in Table 1 below.

| Treatment | Oleic acid (gram) | H2O (mL) | TEOS (gram) | APMS (gram) | HCl (ml) | Mixer time (hour) | Aging time (day) |
|-----------|-------------------|----------|-------------|-------------|----------|-------------------|-----------------|
| IE        | 0.6877            | 150      | 3.8104      | 0.6247      | 10       | 2                 | 4               |
| IIE       | 0.6789            | 150      | 3.7792      | 0.6502      | 15       | 2                 | 4               |
| IIIE      | 0.6818            | 150      | 3.7629      | 0.7073      | 20       | 2                 | 4               |
| IVE       | 0.6707            | 150      | 3.8269      | 0.5160      | 25       | 2                 | 4               |
| VE        | 0.6925            | 150      | 3.8184      | 0.5020      | 30       | 2                 | 4               |

2.4. Synthesis of Silica Mesoporous Material Using Oleic Acid as Template (Addition of TEOS Concentration and Variation of Volume HCl 0.1M)
To determine the effect of increasing TEOS concentrations, TEOS was doubled with the same experimental stages as experiment 2.1 and varying the volume of HCl 0.1M. The conditions reaction can be seen in Table 2 below.

**Table 2. Synthesis of Mesoporous Silica with increased concentration of TEOS and HCl 0.1M**

| Treatment | Oleic acid (mol) | H₂O (mL) | TEOS (gram) | APMS (gram) | HCl (mL) | Mixer time (hour) | Aging time (day) |
|-----------|------------------|----------|-------------|-------------|----------|------------------|------------------|
| 1B        | 1.5116           | 150      | 7.5112      | 1.1048      | 20       | 2                | 4                |
| 2B        | 1.5048           | 150      | 7.5121      | 1.0158      | 30       | 2                | 4                |
| 3B        | 1.5135           | 150      | 7.5031      | 1.0923      | 40       | 2                | 4                |
| 4B        | 1.5066           | 150      | 7.5210      | 1.0923      | 50       | 2                | 4                |
| 5B        | 1.5040           | 150      | 7.5169      | 1.6170      | 60       | 2                | 4                |

3. Results and Discussion

3.1 Synthesis of Silica Mesoporous Material Using Oleic Acid as Template (Reduction of TEOS Concentration and Variation volume of HCl 0.1M).

Oleic acid mixed with aquabides while stirring then added HCl 0.1M and stirred for 1 hour (Mixture A) and generated clear solution. The mixture of tetraethylortosilicate (TEOS) and 3-aminopropyltrimethoxysilane (APMS) was stirred for 5 minutes (mix B) obtained by a white suspension mixture. The B mixture was introduced into mixture A and stirred for 2 hours and obtained a white suspension mixture. The mixture is aged in the oven at 80 °C for 4 days until solid solids are formed. The solids are separated and dried at 50°C. The solids were calcined at 900 °C for 4 hours and obtained white solids. The results obtained vary according to the reaction conditions as shown in Table 3 below.

**Table 3. Product silica with reduce concentration of TEOS and HCl 0.1 M variation**

| Treatment | HCl 0.1 M (mL) | Yield (gram)          |
|-----------|----------------|-----------------------|
| IIE       | 10             | 0.6614                |
| IIE       | 15             | 0.3753                |
| IIIE      | 20             | 0.3011                |
| IVE       | 25             | The silica solid is very little |
| VE        | 30             | The silica solid is very little |

Based on Table 3 the increasing volume of HCl0.1 M (pH of the reaction mixture progressively changed from 5 to 2) with the low concentration of tetraethylortosilicate (TEOS) causing fewer silica mesopores. In the treatment of IVE and V (pH 2) the mesoporous silica solids obtained are so small that they can not be separated from the solvent. This is in accordance with the reference [15] the formation of mesoporous mesophorous material tissue is strongly influenced by the TEOS concentration and pH of the reaction mixture.

The product solids of IIE, IIE and IIIE are characterized by their functional groups using FT-IR as shown in Fig. 1 (a) and the results of X-ray diffraction analysis are shown in Fig. 1 (b) below.
The FT-IR spectrum of product IE, IIE and IIIE in Figure 1(a) shows the absorption peaks at 3448 cm\(^{-1}\) to 3425 cm\(^{-1}\) indicating the presence of \(-\text{Si-OH}\) groups on the surface of the silica material but with low intensity. The absorption peaks at 1103 cm\(^{-1}\) to 1095 cm\(^{-1}\) indicate the presence of \(-\text{Si-O-Si}\) group on silica network [16]. The intensity of the uptake peak is sharper in the presence of an increase in the amount of HCl added, indicating the formation of \(-\text{Si-O-Si}\) network affected by pH.

Diffractogram of X-ray diffraction in Figure 1(b) shows the three mesoporous products of silica showing the same peak of the diffractogram that is widened at an angle of \(2\theta\) between 15\(^\circ\) and 30\(^\circ\). This shows that the three products have an amorphous structure and indicate the particles of silica products have nano size [17].

The porosity of product IE, IIE and IIIE was characterized using a Brunauer-Emmet-Teller (BET) nosophing-isotherm adsorption-adsorption method and pore size was calculated using the Barret-Joyner-Halenda (BJH) method. The adsorption-desorption nitrogen isotherm of the three products shown in Figure 2a and the pore size distribution can be seen in Figure 2b below. The hysteresis form of the IE silica product (black color) and IIE (red color) have hysteresis type H3 due to the presence of nonrigid aggregates of particles such as plat (platlike) having pore-shaped slits. While the silica product IIIB does not have hysteresis so it can be assumed the silica product IIIB has no pores. This is adjusted by reference [18]. The results of BJH analysis on pore size distribution based on graphs of Fig. 2 (b) on IE, IIE and IIIE silica products are classified as mesoporous materials because they have a pore size distribution range between 2-15 nm, as well as the reference [18].
Morphology of silica product IE, IIE, and IIIE characterized using Electron scanning microscopy (SEM) by magnification 2.50K X are shown in Figure 3 below. The silica product IE shows surfaces of sheets having pore cracks (Figure 3 (a)), as well as the silica product IIE showing surfaces in the form of corrugated sheets having pore crevices (Figure 3 (b)). While the silica product IIIE has a thin flat sheet surface and does not have pore cracks (Figure 3 (c)). The morphology of all the silica products according to the isotherm adsorption-desorption graph hysteresis shown in Figure 2 (a).

![SEM images of Silica products](image)

**Figure 3.** SEM image of Silica produk IE (a), IIE (b) dan IIIE (c)

### 3.2. Silica Mesoporous Material Synthesis Using Oleic Acid as Template (Increased TEOS Concentration and HCl Volume Variation 0.1M)

Experiment 2.1 with reduced TEOS concentrations and using 0.1 M HCl 25 ml and 30 ml respectively, very small silica solids were formed. So as to increase the amount of TEOS as much as two-fold and vary the volume of 0.1 M HCl. The amount of silica product obtained after calcination can be seen in Table 4 below.

| Treatment | HCl 0.1M (mL) | Yield (gram) |
|-----------|---------------|--------------|
| 1B        | 20            | 2.0501       |
| 2B        | 30            | 1.9032       |
| 3B        | 40            | 1.2133       |
| 4B        | 50            | 1.0564       |
| 5B        | 60            | 1.3065       |

The FT-IR spectra of the silica product 1B, 2B, 3B, 4B and 5B can be seen in Figure 4(a) and the results of X-ray diffraction analysis are shown in Figure 4(b) below.
The FT-IR spectrum all the silica products in Figure 4(a) show that the Si-O-Si-silica network is formed on the silica material. In the wave number cm⁻¹ to cm⁻¹ (broad) of the OH group of -Si-OH on the silica surface. While the wave number 3464 cm⁻¹ to 3448 cm⁻¹ is caused by asymmetry of Si-OH group (ω₂, Si-OH). The appearance of an absorptive peak in the wave number between 1111 cm⁻¹ to 1103 cm⁻¹ is strong due to the symmetry -Si-O-Si (ω, Si-O-Si) group according to the literature [16].

The width of the X-ray diffractogram of the 1B, 2B, 3B, 4B and 5B silica products in Figure 4(b) shows all the silica products having a widened diffractogram at an angle of 2θ between 15° and 30°. Indicates that the obtained silica material is amorphous and the material has a nano size this is adjusted by reference [17].

![Figure 4](image_url)  
**Figure 4.** Spectrum FT-IR (a) and X-ray diffractograms (b) of silica product 1B, 2B, 3B, 4B and 5B

The results of characterization of isotherm adsorption-desorption of product 1B, 2B, 3B, 4B and 5B can be seen in Figure 5 (a) while the distribution of pore size can be seen in Figure 5 (b) below. The hysteresis adsorption isotherm type of the silica product has a different shape (Figure 5 (a). The hysterical form of the silica product 1B (black color) is classified into Type H4 which has a thin slit pore and is included as a microporous material. Silica product 2B has no hysteresis (color red) shows that the silica product has no pores, whereas silica product 3B (blue color), 4B (purple color) and 5B (green color) have hysteresis type H3, this is due to the nonrigid aggregate of particles such as the plate having pore-shaped pores adjusted by reference [18].

![Figure 5](image_url)  
**Figure 5.** Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of silica products 1B, 2B, 3B, 4B and 5B
Morphology of silica product 1B, 2B, 3B, 4B and 5B characterized using electron scanning microscopy (SEM) by magnification 2.50K X are shown in Figure 5. The silica product 1B shows a porous surface (Figure 5 (a)), the silica product 2B on the surface is more dense and there are spherical particles (Figure 5 (b)), the surface of silica product 3B is flat but has a narrow gap (Figure 5(c)). The silica product 4B has a more hollow surface and there are more gaps and spherical particles (Figure 5(d)). While the silica product 5B has an uneven surface with narrow gaps (Figure 5 (e)).

The morphology of all silica products corresponds to hysteresis of the isotherms adsorption-desorption graph shown in Figure 5(a)

**Figure 6.** SEM images silica product of sample 1B (a), 2B (b), 3B (c), 4B (d) and 5B (e)
4. Conclusions
The synthesis of silica mesoporous material from tetraethylortosilicate (TEOS) as the source of silica, oleic acid as template and 3-aminopropyltrimethoxysilane (APMS) as co-structure directing agents (CDSA) has been performed. The TEOS concentration used affects the amount of silica yield obtained. Reduction of TEOS concentrations and an increase in HCl 0.1M volume resulted in fewer silica products being obtained. While the increasing amount of TEOS used is getting bigger but also decreasing yield with the increase of HCl volume used. All silica products indicate the formation of silica tissue (-Si-O-Si-) and amorphous products. Oleic acid has been able to function as a template it can be proved that there is a hiterisis on desorption adsorption graph although the pore size distribution still varies with range 2-50 nm.

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