

# Effect of Addition of Oleic Acid as a Template with Tetraethylorthosilicate (TEOS) as Source of Silica on Porosity Mesoporous Silica Material

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## ABSTRACT

Mesoporous silica material has been synthesized using tetraethylorthosilicate (TEOS) as a source of silica, oleic acid as a template, and 3-aminopropyltrimethoxysilane (APMS) as co-structure directing agents (CSDA). The synthesis of silica material was made with a variation in the mole ratio of TEOS: Oleic acid with a ratio of 1: 0.2; 1: 0.3; 1: 0.5; 1: 0.6; 1: 0.7; 1: 0.9, and 1: 1. A mixture between TEOS and APMS was added to a mixture of oleic acid, HCl 0.1N and demineralized water then stirred at room temperature for 2 hours. Then aging, the mix at 80°C for 48 hours until solids are formed. Product separation was used in the centrifugation method. The resulting solid was dried at 50°C, and to remove the template, calcined at 550°C for 6 hours. The product of XRD analysis has a wider diffraction peak that indicates an amorphous material. The FT-IR spectrum shows the Si-OH and Si-O-Si groups which are characteristic of silica material. The product of SEM analysis offers the presence of sheets and plates of particle forms with different sizes. Adsorption-desorption isotherm (BET) shows an isotherm type IV curve, and dominant pore sizes are 1.945 and 4.588 nm.

**Keywords:** APMS, Oleic Acid, Silica Mesoporous Material, Templates, TEOS

## ABSTRAK

Material silika mesopori telah disintesis menggunakan tetraetilortosilikat (TEOS) sebagai sumber silika, asam oleat sebagai template dan 3-aminopropyltrimethoxysilane (APMS) sebagai co-structure directing agent (CSDA). Sintesis bahan silika dibuat dengan variasi perbandingan mol TEOS : asam oleat dengan perbandingan 1 : 0,2; 1 : 0,3; 1 : 0,5; 1 : 0,6; 1 : 0,7; 1 : 0,9 dan 1 : 1. Campuran antara TEOS dan APMS ditambahkan ke dalam campuran asam oleat, HCl 0,1N dan air demineralisasi kemudian diaduk pada suhu kamar selama 2 jam. Kemudian tuang campuran tersebut pada suhu 80oC selama 48 jam hingga terbentuk padatan. Pemisahan produk menggunakan metode sentrifugasi. Padatan yang dihasilkan dikeringkan pada suhu 50oC dan untuk menghilangkan template, dikalsinasi pada suhu 550oC selama 6 jam. Hasil analisis XRD memiliki puncak difraksi yang lebih lebar yang mengindikasikan material amorf. Spektrum FT-IR menunjukkan gugus Si-OH dan Si-O-Si yang merupakan karakteristik material silika. Hasil analisis SEM menunjukkan adanya bentuk partikel lembaran dan pelat dengan ukuran yang berbeda. Isoterm desorpsi adsorpsi (BET) menunjukkan kurva tipe IV isoterm dan ukuran pori dominan adalah 1,945 dan 4,588 nm.

**Kata kunci:** APMS, Asam Oleat, Bahan Silika Mesopori, Template, TEOS



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## 1. Introduction

Mesoporous materials have pore diameters between 2 nm and 50 nm. According to IUPAC, porous materials are divided into four categories based on the size of their pore diameter (d), namely (i) microporous (0 - 2 nm), (ii) mesoporous (2 nm - 50 nm), (iii) macroporous (50 nm -7500 nm), (iv) megaspores [1]. The synthesis of mesoporous materials involves guiding the structure to form the desired pore size. One of the materials used to guide the structure is a template. Organic component factors affect the formation of pore templates. The organic materials used are amphiphilic molecules such as surfactants with a molecular structure consisting of a hydrophilic (polar) head group and a hydrophobic (non-polar) carbon chain tail group. Differences in size,

type, shape, functional groups, and molecular template charges can produce different micelles that can form aggregates [2,3]

The interaction between the inorganic and organic components determines the structural characteristics of the silica material. The type of interaction depends on the type of surfactant used, which can be in the form of weak non-covalent bonds such as hydrogen bonds, Van der Waals forces, and electrovalent bonds [4]. The formation of silica material takes place through a sol-gel process in which the solid is obtained through the stages of hydrolysis and condensation reactions from the precursor, then the formation of the sol, the process of gelation (sol-gel transition), the process of maturation (aging) and drying (drying). Hydrolysis and condensation processes are affected by the precursor, alkyl groups, type of catalyst, type of solvent, temperature, pH, and relative concentration of components in the precursor mixture [1].

The synthesis of mesoporous silica materials using surfactants as templates have been carried out by Kleitz et al. (2003) and Khodakov et al. (2005) using nonionic surfactants, namely a mixture of Pluronic P123 triblock copolymers [4,5]. Zhao et al. (1999) used Rigid Bolaform Surfactant cationic surfactants [6]. Yokoi et al. (2003) used anionic surfactant Sodium Dodecyl Sulfate (SDS) [7], Gracia-Bennet et al. (2005) used N-lauroyl glutamic acid [8], Wang et al. (2008) used N-lauroylsarcosine sodium (Sar-Na) [9], and Andriyani et al. used Sodium Ricinoleate [10,11].

Pang et al. (2001) have also researched the effect of citric acid, malic acid, tartaric acid, and lactic acid concentrations as templates in the manufacture of mesoporous silica, where the higher the template concentration, the pore diameter, and volume will generally increase. The use of oleic acid anionic surfactant as a template in synthesizing mesoporous silica materials has not been reported because it is still challenging to determine the right conditions to obtain high pore regularity [12].

Oleic acid is a carboxylic acid group compound with a long aliphatic chain of hydrophilic polar and hydrophobic non-polar so that it can be classified as a surfactant. In the carbon chain (C9 atom), there are double bonds and carboxylic groups, which can affect the formation of micelle aggregates so that they can affect the porous properties of the silica material obtained. Shinya (2014) used oleic acid to manufacture calcium carbonate, which involved the characteristics of the calcium carbonate produced [13].

From the description above, the researcher is interested in researching the synthesis of mesoporous silica materials using oleic acid as a template. In this study, the mole ratio of oleic acid and tetraethylorthosilicate (TEOS) was used with the addition of 0.1 N HCl as a regulator of acidity (pH) and 3-Aminopropyltrimethoxysilane (APMS) as co-structure directing agents (CSDA). The solvent used is demineralized water (deionized water). Then, the silica material is calcined at 550°C to remove the template.

## **2. Materials and Methods**

The tools used in this study include FT-IR spectrophotometer, X-Ray Diffractometer, Surface Area Analyzer, Scanning Electron Microscopy, Furnace control, glassware, oven, hotplate stirrer, digital balance, filter paper, porcelain cup, universal indicator. The materials used in this study included: Tetraethylorthosilicate, 3-Aminopropyltrimethoxysilane, oleic acid, 0.1N HCl, and deionized water.

### *2.1. Research procedure*

As much as 1.49 g of oleic acid was weighed, then 150 ml of demineralized water was added and stirred. Then 30 ml of 0.1 M HCl was added while stirring at room temperature for 1 hour. Then a mixture of 7.5 g TEOS and 1 g APMS was made and stirred for 5 minutes in a closed state. The TEOS and APMS mixture was added to a mixture of oleic acid, HCl, and demineralized water and then stirred for 2 hours. Then it is cooked in the oven at 80°C until a porous solid is formed. Product separation was carried out using centrifugation and dried at 50°C. The resulting solid was calcined at 550°C for 6 hours. The same procedure was carried out for the mole ratio of TEOS: Oleic Acid (1: 0.3), (1: 0.5), (1: 0.6), (1: 0.7), (1: 0.9), and (1: 1). The resulting product was characterized using FT-IR, XRD, SEM and BET analysis.

## **3. Results and Discussion**

### *3.1. Making Mesoporous Silica Material*

Silica mesoporous material was made from tetraethylorthosilicate (TEOS), oleic acid, and 3-aminopropyltrimethoxysilane (3-APMS) with the addition of 30 ml HCl was carried out by varying the

addition of oleic acid starting from 1.49 g, 2.97 g, 4.46 g, 5.95 g, 7.44 g, 8.93 g, 10.42 g with a TEOS mole ratio: Oleic acid is (1: 0.2), (1: 0.3), (1: 0.5), (1: 0.6), (1: 0.7), (1: 0.9) and (1: 1). The resulting silica material product is a white solid after being calcined at 550 °C. Then characterized by FT-IR, XRD, SEM, and BET.

### 3.2. Characterization X-Ray Diffraction (XRD)

The resulting mesoporous silica material was characterized by XRD analysis to identify the shape of the silica to obtain a diffraction pattern of silica at an angle of  $2\theta$ , as shown in Figure 1. Based on the XRD results, it can be seen that the XRD diffractogram at an angle of  $2\theta$  between  $10^\circ$  to  $30^\circ$  shows a widened diffraction peak at  $22.01^\circ$ . The widening of the diffraction peaks indicates that the silica obtained is amorphous. It follows the data [14,15]. Based on the XRD diffractogram, silica is shown at an angle of  $2\theta$  from 20.85, 26.65, 40.29, and  $42.47^\circ$ .

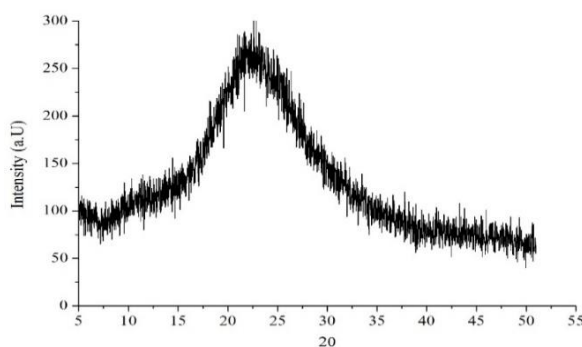


Figure 1. XRD Diffractogram of Mesoporous Silica Material

### 3.3. Characterization FT-IR spectrum

FTIR analyzed the silica material obtained to determine whether functional groups related to silica were formed. The FT-IR spectrum of the calcined mesoporous silica material can be seen in Figure 4, and the spectrum of TEOS and oleic acid used as comparators can be seen in Figure 2 and Figure 3.

The results of the functional group characteristics of the mesoporous silica samples showed that the oleic acid used as a template was lost when calcined. This can be seen from the absence of C=O absorption in the range  $1700-1725\text{ cm}^{-1}$  and C=C absorption in the range  $1640 - 1680\text{ cm}^{-1}$ .

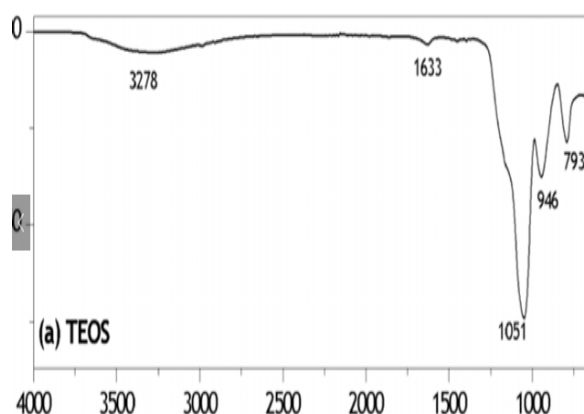


Figure 2. FT-IR spectrum of Tetraethylortho silicate (Wancel et al., 2013)

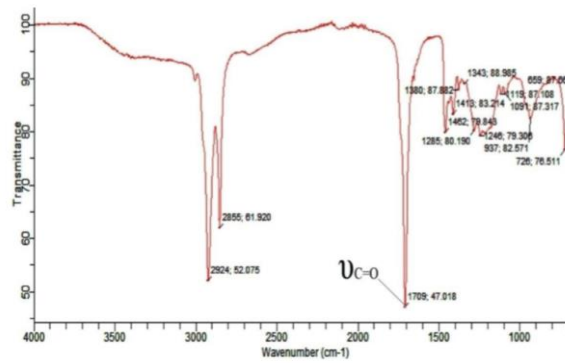


Figure 3. FT-IR spectrum of Oleic Acid

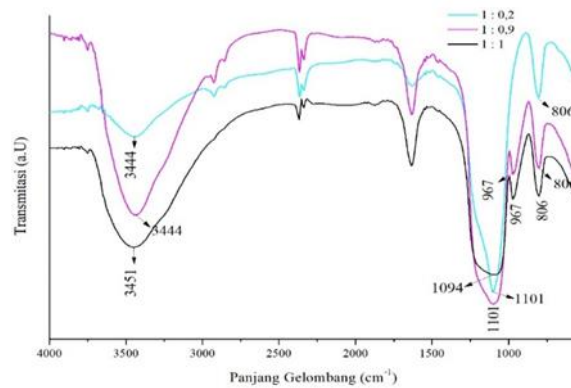


Figure 4. FT-IR Spectrum of Silica Material for Variations in the Addition of TEOS: Oleic Acid (1: 0.2), (1: 0.9) and (1: 1)

FT-IR spectrum data obtained for variations in mole 1: 0.2; 1: 0.9, and 1: 1 are supported by literature data as in Table 1

Table 1. Literature data of absorption peaks of mesoporous silica materials

Functional Groups and Wavenumber (cm <sup>-1</sup> )				References
vas Si-OH	vs Si-O-H	vas Si-O-Si	vs Si-O-Si	
3500	960	1080	810	Zhao, 2011
3500	966	1025	801	Liu, 2010
3458	970	1016	770	Dipowardani, 2008
3700- 3200	910-830	1110-1000	<1000	Silverstein, 1986

Figure 4 it can be seen that there is an absorption peak at wave numbers 3444 cm<sup>-1</sup> – 3451 cm<sup>-1</sup> which is given by the stretching OH group indicating the presence of OH (Si-OH) groups, while at 967 cm<sup>-1</sup>, it is given by the symmetrical group Si-OH. Other absorption peaks seen at wave numbers 1094 cm<sup>-1</sup> - 1011 cm<sup>-1</sup> are due to asymmetric Si-O-Si groups and at 806 cm<sup>-1</sup> are due to symmetrical groups Si-O-Si. The data above follows what is found in the literature. From the description above, it can be concluded that the material formed is silica material.

### 3.3. Characterization Nitrogen Desorption Adsorption Isotherm

To measure the porosity of the mesoporous silica material and the pore size distribution, nitrogen adsorption, and desorption were carried out by isotherm. The isothermal nitrogen adsorption-desorption graph

of mesoporous silica material, as shown in Figure 5, shows the presence of pores in the TEOS variation and the addition of oleic acid ranging from 1: 0.2 to 1: 1. The adsorption-desorption graph of silica material isotherms with a ratio of 1: 0.2 shows a hysteresis loop at a relative pressure ( $P/P_0$ ) between 0.8 – 0.99, while the adsorption-desorption graph of silica material with a ratio of 1: 0.9 shows a hysteresis loop at a relative pressure ( $P/P_0$ ) between 0.66 - 0.995.

In the isothermal nitrogen adsorption-desorption graph, it is identified that mesoporous materials with a ratio of 1: 0.2 and 1: 0.9 were mesoporous materials with Type IV isotherm curves. Where there is a multilayer formation of adsorption and desorption curves according to the IUPAC classification and hysteresis loop. The H3 type is due to the non-rigid aggregate of particles such as plates which have slit-shaped pores [16].

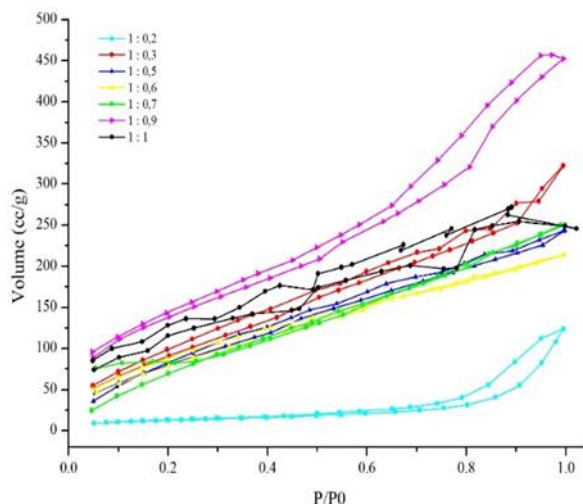


Figure 5. The graph of nitrogen isotherm adsorption-desorption

Adsorption-desorption of nitrogen isotherms also produces a pore-size distribution of silica material, as shown in Figure 6.

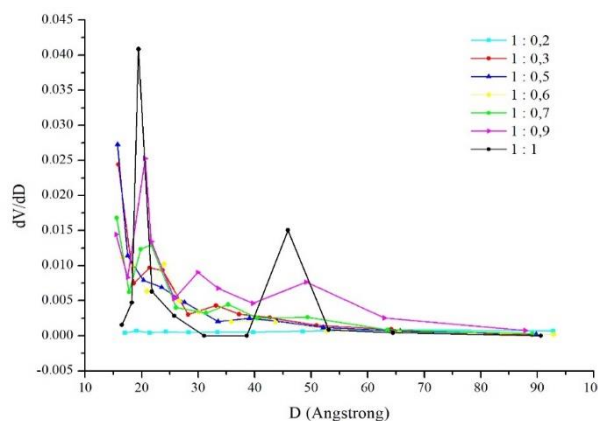


Figure 6. The graph of pore size distribution

Figure 6 shows that the formation of several peaks in the seven samples indicates that the pores formed are still not uniform. The diameter of the resulting pore size is not constant, ranging from 15.45 Å to 92.88 Å or in nanometers 1.54 nm to 9.28 nm so that it can be classified into micropore and mesoporous sizes. In the addition of TEOS and oleic acid with mole ratios of 1: 0.2, 1: 0.3, 1: 0.5, 1: 0.6, and 1: 0.7, the dominant pore size is 19.05 Å, 15.8631 Å, 15.7605 Å, 16.5963 Å and 15.6172 Å which belong to the micropore size. For the 1: 0.9 and 1: 1 variation, the dominant pore size is mesoporous pore size which is 21.684 Å (2.17 nm), while for the 1: 1 oleic variation, the dominant pore size is 19.4527 Å (1.94 nm) and 45.8808 Å (4.588 nm).

The formation of microporous materials in several variations is due to the rough opening of the pore cavities. The pore distribution shows that increasing the template concentration results in larger pore size. It

was because a higher surfactant concentration can form more surfactant micelles. Thus, micelles can print more pores, increasing the specific surface area and total pore volume [17].

### 3.4 Characterization of Nitrogen Adsorption-Desorption Isotherm

Based on the adsorption-desorption nitrogen isotherm (BET) data indicating the presence of pores in the silica material, to determine the morphology of the silica material, an SEM photo analysis was carried out with various magnifications ranging from 1000 – 10,000 times, and the results are as shown in Figure 7.

In Figure 7A, with a magnification of 1000 times, the shape of the silica material particles is not visible, while in Figure 7B, with a magnification of 2500 times, it is clear that the material particles in the form of sheets and plates with non-uniform sizes are arranged to form aggregates. In Figure 7C, with a magnification of 5000, it is clear that between the slab aggregates, you can see cracks or cavities (signs ). Figure 7D with 10000 times magnification shows the same thing as in Figure 7C, but the result looks bigger.

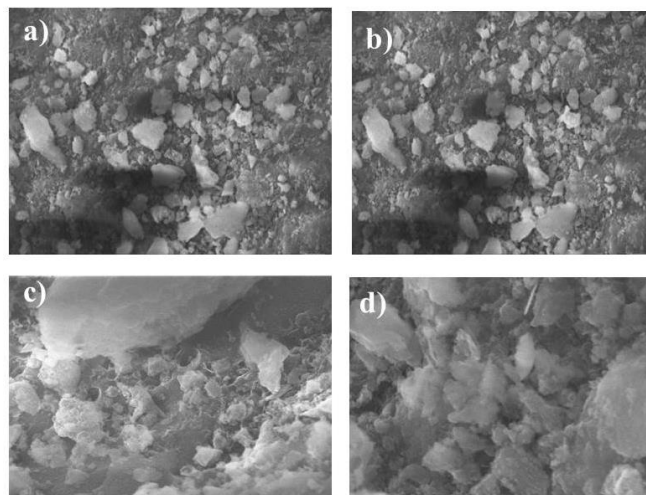


Figure 7. The SEM micrograph of nitrogen adsorption-desorption isotherm of silica material

## 4. Conclusion

The ratio of oleic acid as a template to TEOS as a source of silica affects the final yield of mesoporous silica materials. More templates are added to produce silica products with a coarser texture and smaller mass. And The characteristics of the silica material using XRD showed that there were diffraction peaks that widened at an angle of  $2\theta$  between  $10^\circ - 30^\circ$  which identified that the silica material is amorphous.

## 5. Acknowledgements

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## 6. Conflict of Interest

Authors declare no conflicts of interest

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