# SYNTESIS GLICEROL MONO OLEATE BY SULFATED TITANIA AEROGEL CATALYST

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## ABSTRACT

Glycerol mono oleic (GMO) is a kind of non ionic surfactant, its appearance is light yellow liquid, and it is soluble in a hot alcohol solution, also soluble in chloroform and ether. It also can form emulsion in the water – oil mixed and also as an emulsifier in food. GMO can be obtained from esterification of glycerol and oleic acid, by using solid acid catalyst to form mono glycerin ester. Solid acid catalyst sulfated titania ($TiO_2$-$SO_4^{2-}$) aerogel has been prepared through one-step synthesis by the sol-gel method using sulfuric acid followed by the one-step $CO_2$ supercritical extraction. Highly porous aerogel with a large surface area ($469 m^2/g$) and high porosity (pore volume $1.6 cm^3/g$) has been obtained. The anatase phase is stable after calcination at temperatures up to $700°C$, and the specific surface area, total pore volume and average pore diameter of anatase phase do not change significantly after calcination at $600°C$. Thermally stable and highly acidic sulfated titania aerogel is attractive as catalyst. The catalytic activity of the sulfated anatase shows ability for application as a catalyst for etherification reaction of oleic acid ($C_{18}H_{34}O_2$) with glycerol ($C_3H_8O_3$) to produce glycerol mono oleate.

Key word; Sulfated titania, glycerol mono oleate, sol-gel, supercritical extraction.

## 1. Introduction

Indonesia is a tropical country, which palm is one of the important commodities which contributes to economic development in Indonesia, especially in agro industrial sector. Palm oil estate covered 5.6 million ha (2004) and produced up to 13 million tons of crude palm oil in 2006. Currently, Indonesia is the second largest producer of palm oil in the world. However, according to the prediction of the Oil palm World, Indonesia will be the highest producer of palm oil in 2010. Palm oil has been used as edible or cooking oil for many years. Now, palm oil is also consumed as an industrial raw material. Oleochemical industries, for example consume palm oil as one of their raw materials. On the other side, palm oil is the most important renewable source of raw material in Indonesia. Glycerol mono oleic is a kind of non ionic surfactant, its appearance is light yellow

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liquid, and it is soluble in a hot alcohol solution, also soluble in chlorofom and ether. It also can form emulsion in the water – oil mixed and also as an emulsifier in food. Glycerol mono oleic can be obtained from esterification of glycerol and oleic acid, by using right catalyst to form mono glycerin ester. This surfactant has important role in cosmetic industry, food, beverage, medicine and lubricant due for used as emulsifier and stabilizer.

The optimum process esterification of glycerol with oleic acid using sulfuric acid as catalysts have been studied completely in Research Centre for Chemistry, Indonesian Institute of Sciences, (RCChem-LIPI). The esterification of glycerol mono oleic using sulfuric acid as catalyst happened on several steps, which were: esterification, washing the product and decantation. After the ester was formed, the impurities (catalyst and reactants which are not reacted) in glycerol mono oleic was separated by washing it with hexane and potassium chloride solution, then the product was decanted. Those several steps were done to aim glycerol mono oleic product free from sulfuric acid. While the reaction happened, the catalyst was mixed with reactants and formed a homogeneous solution.

The ideas of studying esterification of glycerol with oleic acid by using solid catalyst are to simplify the processes. The product should not been washed, it can be separated directly after the esterification then have analyzed; therefore the process will be easier. For the industry scale, this idea would give benefit in purification product.

The esterification of glycerol with oleic acid proceeds by the following mechanism:
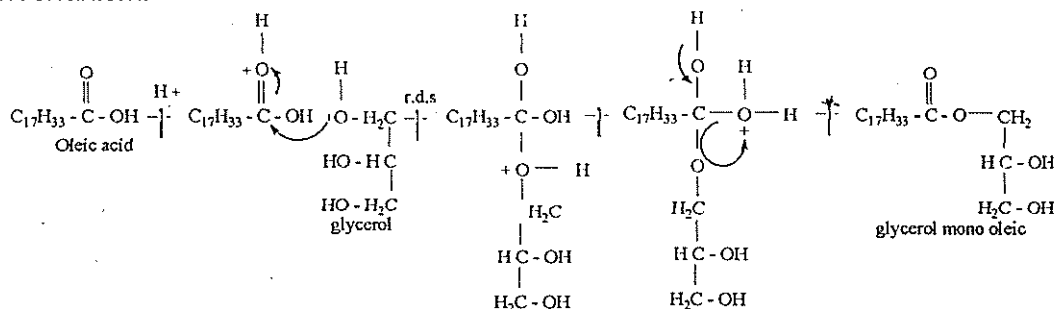


Esterification of the carboxyl group is relatively slow; in order to make the process faster it will need high temperature and catalyst to achieve equilibrium conversion of time.

The acid strengths for the sulfated metal oxides as solid acid catalyst are high. New types of non-zeolite solid superacids, namely single or binary metal oxides ($ZrO_2$, $TiO_2$, $Fe_2O_3$, $TiO_2$–$SiO_2$, $NiO$–$ZrO_2$ etc.) modified by sulfate ions, have been developed [1-7]. These materials exhibit extremely high activities for various acid-catalyzed reactions such as skeletal isomerization of butane, ring-opening isomerization of cyclopropane, alkylation of benzene derivatives, cracking of paraffins, and dimerization of ethylene [8-14]. The sulfated $TiO_2$, in which covalent surface sulfates such as $TiOSO_4$ can be formed by the sulfuric acid treatment, possesses acid centers of high acid strength in the range $-16.04 < H_0 < -14.52$ [1], similar to sulfated zirconia, and has redox sites of $Ti^{4+}/Ti^{3+}$ as well as $SO_4^{2-}$ type. Here $H_0$ is the Hammett acidity function. Ho is used to describe the strength of superacids which is actually equivalent to pH for aqueous solutions. However, the disadvantage of anatase phase $TiO_2$ is its relatively low surface area, usually smaller than $55 m^2/g$ [15], and the poor stability of anatase at high temperatures, stable only below 500°C [16].

The aerogels, prepared by the sol-gel method followed by supercritical drying, consist of nanoparticles and have large surface area and high porosity. The first step in the preparation is the formation of an alcogel through the sol-gel chemistry, hydrolysis and subsequent condensation in alcoholic solutions. For catalytic uses, the solvent must be removed from the gel. During conventional drying, a liquid-vapor interface is formed in the pores, and the corresponding surface tension collapses the oxide network, thereby reducing its porosity and surface area. However, in the supercritical drying process, the liquid solvent is replaced with a supercritical fluid, and the liquid-vapor interface is eliminated. This supercritical fluid can then be safely removed from the pores leaving the oxide network intact. The resulting material, *aerogel*, can have high porosity, >90%, very low density and extremely large surface area [17].

In this paper, we report the one-step synthesis of sulfate-promoted and highly porous titania aerogel. Sulfuric acid was added to the titanium alkoxide precursor solution, and sulfate is included in the oxide network of the alcogel, making a titania-sulfate cogel. This cogel was supercritically dried resulting in highly porous titania-sulfate aerogel. To understand how sulfate promotion generates superacidity, the structure of the sulfate species on the surface of these materials has been determined. The un-sulfated titania aerogel has been prepared with nitric acid catalyst for comparison. The catalytic activities of

resulting materials were evaluated for the esterification of oleic acid with glycerol to produce glycerol mono oleate.

## 2. Experimental procedure

The sulfated-$TiO_2$ wet gel was prepared by hydrolysis of titanium tetra-n-butoxide (TNB), Ti(n-$OC_4H_9$)$_4$, in a methanol solution with sulfuric acid catalyst. The molar ratios used for the synthesis were [TNB]: [$H_2O$]: solvent = 1:13.4:12.7 and [$H_2SO_4$]: [TNB] = 0.06. At first, TNB was dissolved into methanol at room temperature. A mixture of the catalyst solution, remaining methanol, $H_2O$ and $H_2SO_4$, was added to the TNB solution, and then stirred for 1h. The solution gelled in 24h after addition of the catalyst solution. The un-sulfated-$TiO_2$ wet gel was prepared in the same condition using $HNO_3$ as catalyst for hydrolysis. The solution gelled in 2min after addition of the catalyst solution. The gel time was defined as the time required after mixing for the vortex created by the stirring to disappear completely. After aging at room temperature for 24h, the wet gels were supercritically extracted by flowing supercritical carbon dioxide at 60°C and 22Mpa for 4h using a supercritical extraction system (Supercritical Fluid Extraction System, Newport Scientific Inc.)

The specific surface area, pore volume and pore size distribution of the gels, before and after calcination, were estimated by the BET and Barret-Joyner-Halenda (BJH) method [18] using $N_2$ adsorption-desorption curves. Infrared spectra of the sulfated gels were measured by the KBr disc method with a Fourier transform infrared spectrometer (FTIR, BIO-RAD FTS-60A). Crystallization behaviors of the aerogels were investigated by X-ray diffractometry (Rigaku, RAD-C) after calcination at temperatures in the range from 500 to 800°C with a heating rate of 10 °C min$^{-1}$, holding time of 2 h and a cooling rate of 10 °C min$^{-1}$.
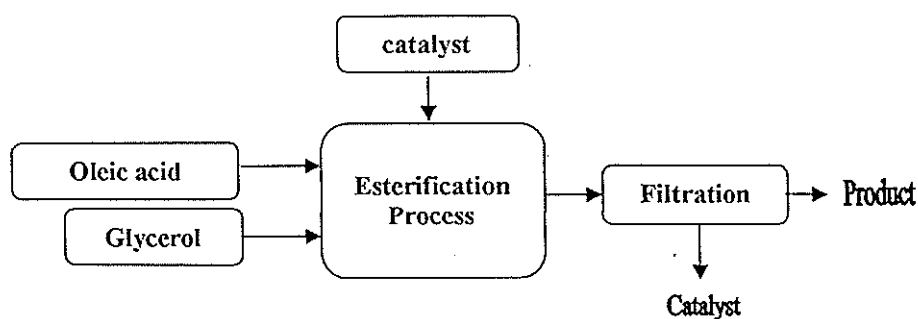


Figure 1. Flow diagram of esterification of glycerol with oleic acid using solid catalyst

Oleic acid, glycerol and sulfated titania or zeolite were charged into the esterification unit. After the desired temperature was reached, the first sample was withdrawn, get cooled, filtrated then analyzed. This moment was considered as the beginning of the process. During the reaction, sampling was performed every one hour for 7h. Each sample was analyzed for its acid saponification values and percentage of the produced esters, conversion of GMO (yield). Experiments were conducted with constant molar ratios of oleic acid and glycerol (1:1) at 180 °C using sulfated titania catalyst.

## 3. Results

Fig. 2 shows the FT-IR spectra of the sulfated gel as-extracted, calcined at 500, 600, 700 and 800°C for 2h in the range from 4000cm$^{-1}$ to 400cm$^{-1}$. The broad absorption band around 3400 cm$^{-1}$ for all samples indicates the OH groups, the occluded water and surface = Ti-OH groups with H-bonding. Infrared spectra of sulfated metal oxides generally show a strong absorption band at 1380-1370cm$^{-1}$ and broad bands at 1250-900cm$^{-1}$ [19]. The former is attributed to the stretching frequency of S=O and the latter bands are the characteristic frequencies of SO$_4^{2-}$. The as-extracted sample shows the presence of the absorption bands in the range from 1250 to 900cm$^{-1}$, 1250, 1128, 1058, and 900cm$^{-1}$, and strong peaks at 1635cm$^{-1}$ and at 1461cm$^{-1}$, attributed to the characteristic frequencies of SO$_4^{2-}$, and stretching of -OH and vibration of -C-H, respectively. After calcination at 500°C, the peak at 1461cm$^{-1}$ disappeared, but the peaks at 3400cm$^{-1}$ and at 1635cm$^{-1}$ ascribed to OH group still existed and strong peak at 583cm$^{-1}$ attributed to metal-oxygen bonds of Ti-O was found.
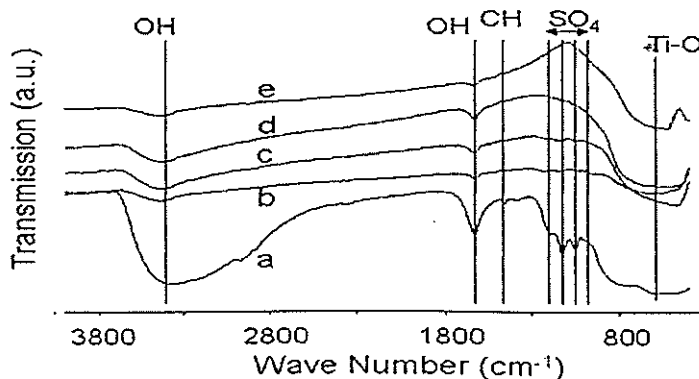


Figure 2. IR absorption spectra of sulfated titania aerogel after calcination at various temperatures (a) as-prepared, (b) 500°C, (c) 600°C, (d) 700°C, and (e) 800°C

The X-ray powder diffraction pattern for the sulfated titania aerogel calcined at 500°C shows the diffraction peaks of anatase (Fig. 3-1b). The anatase structure was stable after calcination up to 700°C (Fig. 3-1d). After calcination at 750°C, small peaks of rutile structure began to found (Fig. 3-2). After calcination at 800°C, the diffraction peaks of anatase disappeared (Fig.3-1e).

The X-ray diffraction peaks of anatase were found for the un-su''ated titania aerogel as-extracted (Fig. 4a). The anatase structure was stable after calcination at temperatures up to 500°C (Fig. 4b). After calcinations at 600°C, the small diffraction peaks of rutile were found (Fig. 4c). After calcination at 700°C, the anatase peaks disappeared (Fig. 4d).
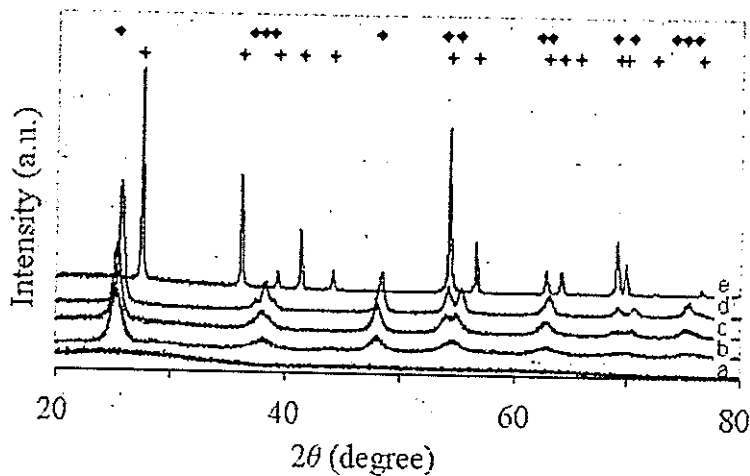


Figure 3-1    XRD patterns of sulfated titania aerogel; (a) as-extracted, (b) 500°C, (c) 600°C, (d) 700°C and (e) 800°C. ◆ ; anatase    + ; rutile
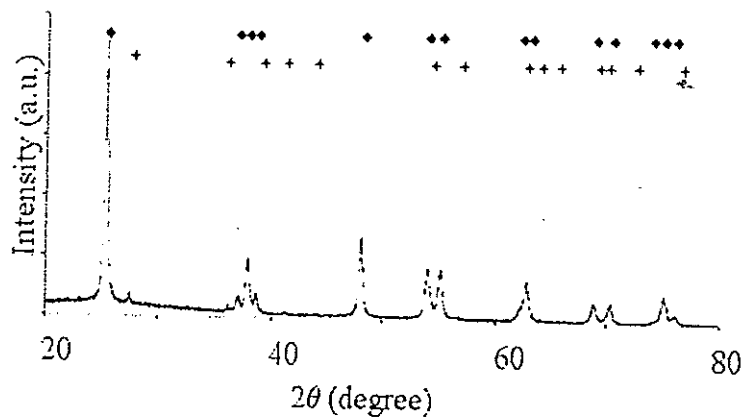


Figure 3-2 XRD patterns of sulfated titania aerogel after calcination at 750°C
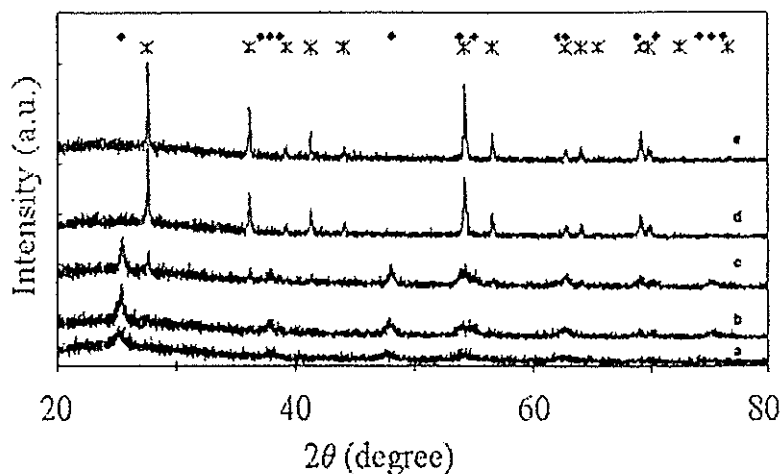◆ ; anatase    + ; rutile

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Figure 4 XRD patterns of un-sulfated titania aerogel; (a) as-extracted, (b) 500°C, (c) 600°C, (d) 700°C and (e) 800°C. ◆ ; anatase    * ; rutile

Table 1 shows the specific surface area, cumulative pore volume and average pore diameter of the sulfated- and the un-sulfated $TiO_2$ gels as-extracted and after calcination at various temperatures for 2h. The specific surface area, average pore diameter and pore volume of the as-extracted sulfated titania aerogel were $469 m^2 g^{-1}$, $11.9 nm$ and $1.60 cm^3 g^{-1}$, respectively. The specific surface area and the pore volume of the sulfated titania are larger than those of the un-sulfated titania, $195 m^2 g^{-1}$ and $0.55 cm^3 g^{-1}$, respectively, more than two and three times, respectively (Table 1).

Table1 1. Specific surface area, cumulative pore volume, and average pore diameter of the titania gels after calcination at various temperatures. [a]

| | As-extracted gels | 500°C | 600°C | 700°C | 800°C |
|---|---|---|---|---|---|
| **TiO$_2$-SO$_4$ Aerogel** | | | | | |
| Surface area (m$^2$g$^{-1}$) | 469 | 175 | 117 | 65 | 7 |
| Pore volume (cm$^3$g$^{-1}$) | 1.60 | 0.94 | 0.74 | 0.40 | 0.07 |
| Average pore diameter (nm) | 11.9 | 19.1 | 24 | 21 | 39.7 |
| **TiO$_2$ Aerogel** | | | | | |
| Surface area (m$^2$g$^{-1}$) | 195 | 90 | 58 | 19 | 5 |
| Pore volume (cm$^3$g$^{-1}$) | 0.55 | 0.49 | 0.35 | 0.16 | 0.05 |
| Average pore diameter (nm) | 12.8 | 18.7 | 20.0 | 36.5 | 51.6 |

a , The accuracy of $N_2$ adsorption measurements was 0.1%, and the reproducibility of these values for each sample was within 10%.

After calcination at 500°C, the specific surface area and the pore volume of the sulfated titania, about $175m^2g^{-1}$ and $0.94cm^3g^{-1}$, are two times larger than those of the un-sulfated titania. After calcination at 600°C, the specific surface area and pore volume of the sulfated titania, about $117m^2g^{-1}$ and $0.74cm^3g^{-1}$, are two times larger than those of the un-sulfated titania. After calcination at 700°C, the specific surface area and pore volume of the sulfated titania, about $65m^2g^{-1}$ and $0.4cm^3g^{-1}$, are more than three and two times larger than those of the un-sulfated titania, respectively. After calcination at 800°C, the specific surface area and the pore volume of the sulfated titania are almost the same as those of the un-sulfated titania Table 1). The specific surface area and the cumulative pore volume of the sulfated titania were much larger than those of the un-sulfated titania, and gradually decreased with increasing calcination temperature up to 700°C. The average pore size of the sulfated and the un-sulfated titania aerogels increased with increasing calcination temperature (Table 1).

Figure 5 shows the effect of activation temperature of the sulfated titania (catalyst concentration Ω 75 %) on the catalytic activity for the reaction of oleic acid with glycerol to produce glycerol mono oleate at 180°C.
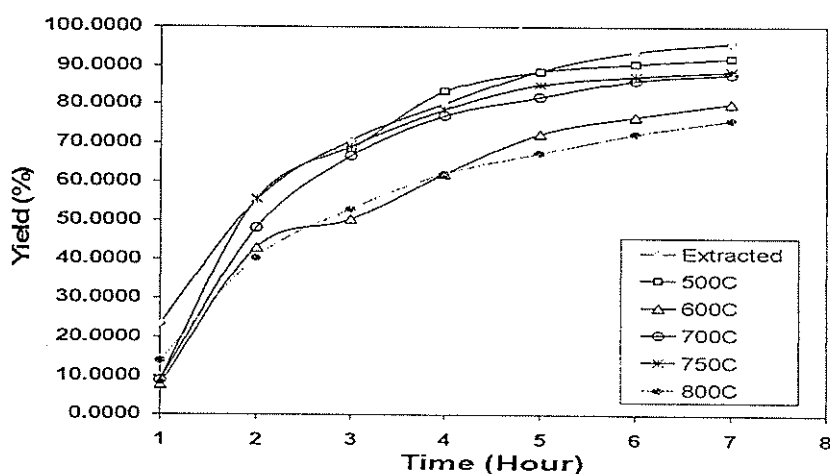


Figure 5 Effect of activation temperatures of the sulfated titania on the catalytic activity on production of glycerol mono oleate

## 4. Discussion

The specific surface area of the sulfated and un-sulfated titania aerogel (Table 1) are as large as those of the usual titania aerogels, e.g. the specific surface area was about 160 $m^2g^{-1}$ for the as-dried aerogel prepared by supercritical drying in ethanol [19]. The simple process of one-step $CO_2$ supercritical extraction of titania gels is as good as the usual supercritical drying

method. The advantage of this method is a simple one-step-process, and it needs shorter processing time, safety and low cost. The direct extraction of solvent in wet gels with supercritical $CO_2$ will be a good alternative method for the usual "aerogel" method.

Anatase nanoparticles are found for the as-extracted aerogel as discussed previously [20] (Fig. 4a). On the other hand, the sulfated gel is amorphous as-extracted. The infrared absorption bands 1250, 1128, 1058, and 900 $cm^{-1}$ are found for the as-extracted sulfated titania aerogel, and they are assigned to the bidentate sulfate [14] coordinated to $Ti^{4+}$, indicating the formation of titanium sulfate, $Ti_2SO_4$(Scheme 1). The crystallization of anatase is restrained by the formation of sulfate phase.
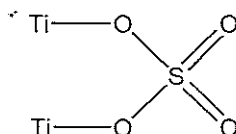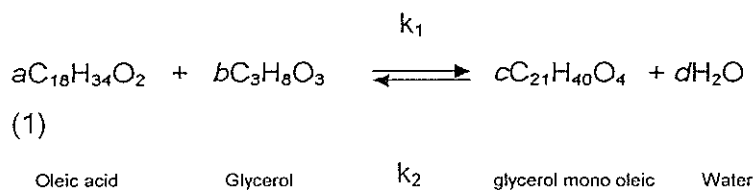


Scheme 1 Bridged bidentate (Dehydrate form)

The pore volume of the un-sulfated aerogel drastically decreased to 0.35$cm^3g^{-1}$ after calcination at 600°C, and that of the sulfated aerogel drastically decreased to 0.40$cm^3g^{-1}$ after calcination at 700°C (Table 1). The average pore diameter of the un-sulfated aerogel increased to 20nm after calcination at 600°C, and that of the sulfated aerogel decreased to 21 nm after calcination at 700°C, and the specific surface area of the un-sulfated aerogel decreased to 58$m^2g^{-1}$, and that of the sulfated aerogel decreased to 65$m^2g^{-1}$(Table 1). The diffraction peaks of rutile are found after calcination of the un-sulfated aerogel at 600°C (Fig. 4c). With the phase transformation from anatase to rutile, the increase in grain size and pore size and the further decrease in surface area are observed (Table 1). After calcination at temperatures higher than 700°C, no peaks of anatase can be found (Fig. 4, d and e). The specific surface area dropped to 19 $m^2g^{-1}$ and average pore size increased drastically to 36.5nm after calcination of the un-sulfated aerogel at 700°C. The diffraction peaks of rutile are found after calcinations of the sulfated aerogel at 750°C (Fig. 3-2). The specific surface area dropped to 7$m^2g^{-1}$ and average pore size increased drastically to 39.7nm at 800°C for the sulfated aerogel, due to the grain growth of rutile crystals (Table 1). The anatase phase in the sulfated gel is thermally stable at higher temperatures, up to 700°C, than in the un-sulfated gel. After calcination at 500°C, the absorption bands attributed to sulfate become weak, but they are still observed

after calcination at 700°C (Fig. 2). The grain growth of anatase in the sulfated aerogel was restrained by the sulfation, and the phase transformation from anatase to rutile was retarded. After calcination at 500°C, the peak at $1461cm^{-1}$, attributed to the vibration of -C-H, disappeared, but the peaks at $3400cm^{-1}$ and at $1635cm^{-1}$ ascribed to OH group still existed. These results show that the organic residue can be eliminated by calcination at 500°C, but OH group remains as well as the sulfate phase.

The IR absorption peaks in the range from 900 to $1250cm^{-1}$, attributed to $SO_4$ group, are not found after calcinations at 800°C. The decomposition temperature of the specific sulfate phase of the sulfated aerogel is much higher than that of the sulfated $TiO_2$ prepared by the sol-gel and impregnation method, 540°C [20]. This result is attractive from the catalytic view point, and the difference may be attributed to the difference in the structure of sulfate phases. Sulfate ion is adsorbed on titania gel by the impregnation method. On the contrary, the specific sulfate is formed by the sol-gel reaction using sulfate catalyst. In addition, decomposition of the sulfate in small pores proceeds at high temperatures like organics residues in gels. The acidity and acid strength of sulfated $TiO_2$ catalysts have been well studied [5, 6, and 21]. In general, a considerable number of Brønsted and Lewis acid sites are formed by modifying $TiO_2$ with $H_2SO_4$. In terms of the Hammett acidity parameter, $H_0$, the acid strengths of these modified catalysts are typically more negative than -14.5, which makes these catalysts stronger than 100% $H_2SO_4$ ($H_0$ = -11.93). Formation of such superacid sulfated $TiO_2$ catalysts has been attributed to the inductive effect of the S=O bonds of the surface sulfate complex. These superacid properties have been considered to be responsible for the high catalytic activity of catalysts modified with sulfuric acid in various acid-catalyzed reactions such as the skeletal isomerization of butane, ring-opening isomerization of cyclopropane, alkylation of benzene derivatives, cracking of paraffins, and dimerization of ethylene [8–14].

The reaction of esterification of glycerol with oleic acid using solid catalyst followed the same kinetics of esterification using sulfuric acid, also followed the kinetics of esterification of Levulinic acid with butanol [22] and kinetics of esterification of stearic acid with glycerol [23]. The basic reaction is represented by the following stoichiometric equation:

$$aC_{18}H_{34}O_2 \ + \ bC_3H_8O_3 \ \overset{k_1}{\underset{k_2}{\rightleftarrows}} \ cC_{21}H_{40}O_4 \ + dH_2O$$

(1)

Oleic acid      Glycerol        glycerol mono oleic     Water

Where $k_1$ is the forward reaction rate constant and $k_2$ is the reverse reaction rate constant. According to equation (1) it is assumed that the reaction between glycerol with oleic acid is an elementary reversible reaction. Elementary reaction is a reaction between one molecule reactant with one molecule reactant. If the rate equation corresponds to a stoichiometric equation are called elementary reactions. The molecularity of an elementary reaction is the number of molecules involved in the reaction, and this has been found to have the values of one, two and occasionally three, note that the molecularity refers only to an elementary reaction, the order reaction is equal with coefficient stoichiometric reaction in elementary reaction [24]. In elementary reaction the molecularity is equal with total order reaction.

Oleic acid reacts readily with glycerol in the presence of catalytic amount of sulfated titania acids to yield compounds called Glycerol mono oleate (GMO)(Fig. 5). The as-prepared sulfated $TiO_2$ aerogel shows the high activity. The catalytic activity of the sulfated anatase shows ability for application as a catalyst for etherification reaction of oleic acid ($C_{18}H_{34}O_2$) with glycerol ($C_3H_8O_3$) to produce glycerol mono oleate.

## 5. Conclusions

Sulfated titania ($TiO_2$-$SO_4^{2-}$) aerogel has been prepared through the one-step synthesis by the sol-gel method using sulfuric acid as hydrolysis catalyst followed by the one-step $CO_2$ supercritical extraction.

(1)    Anatase phase in the sulfated aerogel is stable up to 700°C. The porous structure of the sulfated aerogel is thermally stable in comparison with the un-sulfated aerogel. The sulfate phase, bridged bidentate $Ti_2SO_4$, restrains the crystallization and the grain growth of anatase, and retards the phase transformation from anatase to rutile.

(3)    The catalytic activity of the sulfated titania shows ability for esterification reaction of oleic acid ($C_{18}H_{34}O_2$) with glycerol ($C_3H_8O_3$) to produce glycerol mono oleate.

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