PREPARATION OF SULFATED TITANIA AEROGEL FOR GLICEROL MONO OLEATE SYNTESIS COMPARED TO ZEOLITE

Silvester Tursiloadi and Savitri

Research Center for Chemistry, Indonesian Institute of Sciences, Kawasan PUSPIPTEK, Serpong, Tangerang 15314, Indonesia, E-mail : tursilo@gmail.com

Abstract

Sulfated titania (TiO2-SO42-) aerogel has been prepared through one-step synthesis by the sol-gel method using sulfuric acid as catalyst followed by the one-step CO2 supercritical extraction. Highly porous aerogel with a large surface area (469m2/g) and high porosity (pore volume 1.6cm3/g) has been obtained. Thermal evolution of the gels were evaluated by TGA-DTA, N2 adsorption, TEM and XRD, and the IR absorption spectra measurements were made to discuss the structure of sulfated titania. The anatase phase is stable after calcination at temperatures up to 700oC, and the specific surface area, total pore volume and average pore diameter of anatase phase do not change significantly after calcination at 600oC. Thermally stable and highly acidic sulfated titania aerogel is attractive as catalyst. The catalytic activity of the sulfated anatase shows better ability than Zeolite for application as a catalyst for etherification reaction of oleic acid (C18H34O2) with glycerol (C3H8O3) to produce glycerol mono oleate.

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

1. Introduction

Glycerol mono oleic 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. 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. H_o 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 55m2/g [15], and the poor stability of anatase at high temperatures, stable only below 500oC [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 compared with Zeolite 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-OC4H9)4, in a methanol solution with sulfuric acid catalyst. The molar ratios used

for the synthesis were [TNB]: [H2O]: solvent = 1:13.4:12.7 and [H2SO4]: [TNB] = 0.06. At first, TNB was dissolved into methanol at room temperature. A mixture of the catalyst solution, remaining methanol, H2O and H2SO4, 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-TiO2 wet gel was prepared in the same condition using HNO3 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 60oC and 22Mpa for 4h using a supercritical extraction system (Supercritical Fluid Extraction System, Newport Scientific Inc.)

Changes in the nanostructure of the aerogel during heating were evaluated using thermogravimetric and differential thermal analyses (TG-DTA, Seiko Exstar 6000 TG/DTA 6200 system) and N2 adsorption measurements (Quantachrome, Autosorb). TG-DTA measurements were carried out under airflow of 300 ml min-1, with a heating rate of 10oC min-1. 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 N2 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). The grain size of the samples was estimated from the images observed by a transmission electron microscope (TEM, Philips, TECNAI F20). Crystallization behaviors of the aerogels were investigated by X-ray diffractometry (Rigaku, RAD-C) after calcination at temperatures in the range from 500 to 800oC with a heating rate of 10°Cmin-1, holding time of 2h and a cooling rate of 10°Cmin-1.

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 different temperatures (160 oC, 170 oC, 180 oC, 190 oC) using sulfated titania or zeolite catalysts.

- Glycerol

- Esterification Process

- FiltrationProductCatalyst

- Oleic acid

- catalyst

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

3. Results

TG-DTA profiles of the sulfated and un-sulfated aerogel are given in Fig. 2. For the sulfated aerogel (Fig. 2a), a broad endothermic peak with gradual weight losses about 10% at 100oC, a sharp exothermic peak and a weight loss about 10% at 240oC were observed. A broad and small exothermic peak at 400 oC and a small exothermic peak at 500oC accompanied with a gradual

weight loss were observed. The total weight loss at temperatures up to 750oC was about 40%, and practically no more weight loss was observed at temperatures higher than 750oC. For the un-sulfated aerogel (Fig. 2b), weight loss about 5% was observed around 80oC. In the temperature range between 150 and 400oC, several small exothermic peaks and a gradual weight loss about 10% were observed. Beyond 400oC, the un-sulfated aerogel practically lose no more weight.

Figure. 2 TG-DTA profile of (a) sulfated titania aerogel and

(b) Un-sulfated aerogel

    Fig. 3 shows the FT-IR spectra of the sulfated gel as-extracted, calcined at 500, 600, 700 and 800oC 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 SO42-. 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 SO42-, and stretching of -OH and vibration of -C-H, respectively. After calcination at 500oC, 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 3. IR absorption spectra of sulfated titania aerogel after calcination at various temperatures (a) as-prepared, (b) 500oC, (c) 600oC, (d) 700oC, and (e) 800oC

    The X-ray powder diffraction pattern for the sulfated titania aerogel calcined at 500oC shows the diffraction peaks of anatase (Fig. 4-1b). The anatase structure was stable after calcination up to 700oC (Fig. 4-1d). After calcination at 750oC, small peaks of rutile structure began to found (Fig. 4-2). After calcination at 800oC, the diffraction peaks of anatase disappeared (Fig.4-1e).

    The X-ray diffraction peaks of anatase were found for the un-sulfated titania aerogel as-extracted (Fig. 5a). The anatase structure was stable after calcination at temperatures up to 500oC (Fig. 5b). After calcinations at 600oC, the small diffraction peaks of rutile were found (Fig. 5c). After calcination at 700oC, the anatase peaks disappeared (Fig. 5d).

Figure 4-1 XRD patterns of sulfated titania aerogel; (a) as-extracted, (b) 500oC, (c) 600oC, (d) 700oC and (e) 800oC.

; anatase

; rutile

Figure 4-2 XRD patterns of sulfated titania aerogel after calcination at 750oC

; anatase ; rutile

Figure 5 XRD patterns of un-sulfated titania aerogel; (a) as-extracted, (b) 500oC, (c) 600oC, (d) 700oC and (e) 800oC. ; anatase * ; rutile

Figs. 6-10 show the TEM images and electron diffraction patterns of sulfated and un-sulfated TiO2 aerogels; as-extracted, calcined at 500, 600, 700, 750 and 800oC, respectively. The as-extracted sulfated titania aerogel is in aggregate form and amorphous (Fig. 6a). For the as-extracted un-sulfated titania aerogel, many small crystalline particles were observed (Fig. 6b). The electron diffraction pattern also showed crystals with d = 0.362nm. The particle size of the un-sulfated TiO2 aerogel as-extracted was ca. 5nm in diameter (Fig. 6b). After calcination at 500oC, the small particles ca. 10nm in diameter with d = 0.353nm were found for the sulfated titania aerogel (Fig. 7a), and the particle size of the un-sulfated titania aerogel did not increase significantly, namely ca. 13nm (Fig. 7b). After calcination at 600oC, the particle size of sulfated titania increased to ca. 20nm (Fig. 8a), and two kinds of particles with different particle sizes, ca. 13nm with d = 0.351nm and ca. 25nm in diameter with d = 0.323nm, were found for the un-sulfated titania, (Fig.8b). After calcination at 700oC, the rectangular grains with the length ca. 24nm and the width 15nm with d = 0.352nm were found for the sulfated titania (Fig. 9a). On the other hand, the particle size of un-sulfated titania increased drastically up to 90nm and the hexagonal form with d = 0.324nm was observed clearly (Fig. 9b). After calcinations of the sulfated aerogel at 750oC, two kinds of crystalline particles, one in the rectangular form with length and width are ca. 24 and 15nm, respectively, and the other large grains ca. 50nm in diameter, were observed clearly (Fig. 10). 5nm

Figure 6 TEM image and electron diffraction pattern of (a) sulfated and

(b) Un-sulfated titania aerogel as-extracted

Figure 8 TEM images of the (a) sulfated and (b) un-sulfated aerogel after calcination at 600oC

Figure 7 TEM images of (a) sulfated and (b) un-sulfated aerogel

after calcination at 500oC

Figure 9 TEM image of (a) sulfated and (b) un-sulfated aerogel after calcination at 700oC

Figure 10 TEM image of sulfated aerogel after calcination at 750oC

Table 1 shows the specific surface area, cumulative pore volume and average pore diameter of the sulfated- and the un-sulfated TiO2 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 469m2g-1, 11.9nm and 1.60cm3g-1, respectively. The specific surface area and the pore volume of the sulfated titania are larger than those of the un-sulfated titania, 195m2g-1 and 0.55cm3g-1, respectively, more than two and three times, respectively (Table 1). After calcination at 500oC, the specific surface area and the pore volume of

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

51.6

36.5

20.0

18.7

12.8

Average pore diameter (nm)

0.05

0.16

0.35

0.49

0.55

Pore volume (cm3g-1)

5

19

58

90

195

Surface area (m2g-1)

TiO2 Aerogel

39.7

21

24

19.1

11.9

Average pore diameter (nm)

0.07

0.40

0.74

0.94

1.60

Pore volume (cm3g-1)

7

65

117

175

469

Surface area (m2g-1)

TiO2-SO4 Aerogel

800°C

700°C

600°C

500°C

As-extracted gels

a , The accuracy of N2 adsorption measurements was 0.1%, and the reproducibility of these values for each sample was within 10%.

the sulfated titania, about 175m2g-1 and 0.94cm3g-1, are two times larger than those of the un-sulfated titania. After calcination at 600oC, the specific surface area and pore volume of the sulfated titania, about 117m2g-1 and 0.74cm3g-1, are two times larger than those of the un-sulfated titania. After calcination at 700oC, the specific surface area and pore volume of the sulfated titania, about 65m2g-1 and 0.4cm3g-1, are more than three and two times larger than those of the un-sulfated titania, respectively. After calcination at 800oC, 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 700oC. The average pore size of the sulfated and the un-sulfated titania aerogels increased with increasing calcination temperature (Table 1).

Figure 11. Effect of variation in zeolite catalyst concentration on establishment of equilibrium (mole ratio 1; temperature 180 oC)

Figure 12 Effect of reaction temperatures of the Zeolite on the catalytic activity on production of glycerol mono oleate

Figure 13 Effect of activation temperatures of the sulfated titania on the catalytic activity on production of glycerol mono oleate

4. Discussion
4.1 One-step supercritical extraction and microstructure

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 m2g-1 for the as-dried aerogel prepared by supercritical drying in ethanol [19]. The simple process of one-step CO2 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 CO2 will be a good alternative method for the usual "aerogel" method.

4.2 Thermal evolution of titania aerogels (Crystallization phase transformation and changes in microstructure)

Solvent and other organic residue in the un-sulfated aerogel can be eliminated at temperatures up to 400oC (Fig. 2b). The first two weight losses observed for the sulfated aerogel, about 100oC accompanied with a small endothermic peak and up to 250oC accompanied with a strong exothermic peak, can be attributed to the evaporation and combustion of the solvent ethanol and sulfuric acid residue (Fig. 2a). Anatase nanoparticles are found for the as-extracted aerogel as discussed previously [20] (Fig. 5a and Fig. 6b). 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 Ti4+, indicating the formation of titanium sulfate, Ti2SO4(Scheme 1). The crystallization of anatase is restrained by the formation of sulfate phase. After calcinations at 500oC, anatase particles, 5-10nm in diameter, are found (Fig. 7a). A small exothermic peak around 500oC for the sulfated titania aerogel (Fig. 2a) is attributed to the crystallization. The grain growth of anatase, resulting in the decrease of surface area and the increase in pore size, is observed after calcination of the un-sulfated aerogel at 500oC (Fig. 7b). On the other hand, the grain growth of anatase is observed for the sulfated aerogel after calcinations at 600oC. When the calcination temperature is same, the grain size in the

Scheme 1 Bridged bidentate (Dehydrate form)

sulfated aerogel is smaller than in the un-sulfated aerogel (Figs. 7-.9). The pore volume of the un-sulfated aerogel drastically decreased to 0.35cm3g-1 after calcination at 600oC, and that of the sulfated aerogel drastically decreased to 0.40cm3g-1 after calcination at 700oC (Table 1). The average pore diameter of the un-sulfated aerogel increased to 20nm after calcination at 600oC, and that of the sulfated aerogel decreased to 21 nm after calcination at 700oC, and the specific surface area of the un-sulfated aerogel decreased to 58m2g-1, and that of the sulfated aerogel decreased to 65m2g-1(Table 1). The diffraction peaks of rutile are found after calcination of the un-sulfated aerogel at 600oC (Fig. 5c), and rutile particles are observed by TEM (Fig. 8b). 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 700oC, no peaks of anatase can be found (Fig. 5, d and e). The specific surface area dropped to 19 m2g-1 and average pore size increased drastically to 36.5nm after calcination of the un-sulfated aerogel at 700oC. The diffraction peaks of rutile are found after calcinations of the sulfated aerogel at 750oC (Fig. 2). The specific surface area dropped to 7m2g-1 and average pore size increased drastically to 39.7nm at 800oC 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 700oC, than in the un-sulfated gel. After calcination at 500oC, the absorption bands attributed to sulfate become weak, but they are still observed after calcination at 700oC (Fig. 3). The grain growth of anatase in the sulfated aerogel

was restrained by the sulfation, and the phase transformation from anatase to rutile was retarded. For the sulfated aerogel, gradual weight loss, about 30%, continues in the temperature range from 350 to 750oC (Fig. 2a), and small exothermic peaks about at 400 and 500oC are observed. After calcination at 500oC, 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 500oC, but OH group remains as well as the sulfate phase.

A gradual weight loss of the sulfated aerogel continues at temperatures up to 750oC, and this is attributed to the decomposition of specific sulfate phase. The IR absorption peaks in the range from 900 to 1250cm-1, attributed to SO4 group, are not found after calcinations at 800oC. The decomposition temperature of the specific sulfate phase of the sulfated aerogel is much higher than that of the sulfated TiO2 prepared by the sol-gel and impregnation method, 540oC [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 TiO2 catalysts have been well studied [5, 6, and 21]. In general, a considerable number of Brønsted and Lewis acid sites are formed by modifying TiO2 with H2SO4. In terms of the Hammett acidity parameter, H0, the acid strengths of these modified catalysts are typically more negative than -14.5, which makes these catalysts stronger than 100% H2SO4 (H0 = -11.93). Formation of such superacid sulfated TiO2 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].

At temperatures higher than 800oC, slight increase in weight is observed for both of the aerogel (Fig. 2a), and this is attributed to the oxidation of titania with the phase transformation from anatase to rutile.

4.3 Activity test reaction

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:

$$k1$$

$$aC18H34O2 + bC3H8O3 \rightleftharpoons cC21H40O4 + dH2O \quad (1)$$
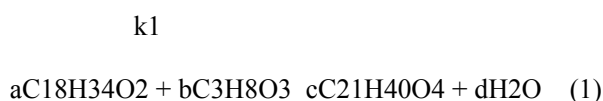
Oleic acid   Glycerol k2 glycerol mono oleic   Water

Where k1 is the forward reaction rate constant and k2 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.

Figure 11 shows the effect of amount of catalyst. The experiments were done several times by using variety catalyst concentration at constant temperature process. From the literature, the establishment of equilibrium accelerates with the increase of concentration of catalyst. The reaction still preceded even there was no catalyst but the reaction rate was very low. By giving catalyst, the temperature process can be lower and time process can be shorter too. ZSM – 5 worked optimum at catalyst concentration 0.75 % of the whole reactants concentration, it gave the biggest conversion of glycerol mono oleic at temperature 180 oC and the time process was 6 hours. When the catalyst concentration was raised to 1% and 2%, the conversions of glycerol mono oleic were lower than the 0.75% catalyst concentration (at the same temperature and the same time). It could happen because of the amount of catalyst were too much, and the catalyst were not mixed very well with the reactants, they precipitate at the bottom of the flask. If the conversion of esterification glycerol mono oleic using zeolite (as catalyst) had compared with the conversion of esterification glycerol mono oleic using sulfuric acid, the sulfuric acid as catalyst gave higher conversion. It could be sulfuric acid being homogeneous catalyst gave hydrogen ions in the solution more easily and thus resulted in higher conversion. But using solid catalyst in esterification process could be more effective in reactive distillation method. The effect of temperature process was studied by varying the reaction temperature at optimum zeolite catalyst concentration. When the temperature process increases, the equilibrium will be achieved sooner as we can see at figure 12. The esterification process of glycerol mono oleic gave high conversions if the temperature process was higher than 170 oC. When temperature process was 190 oC, the equilibrium was achieved after three hours and after six hours the conversion of glycerol mono oleic was 81 %. The curve of 180 oC showed that equilibrium reaction was also achieved after three hours and the conversion of glycerol mono oleic was similar with the conversion at temperature process 190 oC.

Fig. 13 shows the effect of activation temperature of the sulfated titania (catalyst concentration 0.75 %) on the catalytic activity for the reaction of oleic acid with glycerol to produce glycerol mono oleate at 180 oC. Oleic acid reacts readily with glycerol in the presence of catalytic amount of sulfated titania acids to yield compounds called Glycerol mono oleate (GMO). The as-prepared sulfated TiO_2 aerogel shows the high activity. The catalytic activity of the sulfated anatase shows better ability than zeolite 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 700oC. 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 better ability than zeolite for esterification
reaction of oleic acid (C18H34O2) with glycerol (C3H8O3) to produce glycerol mono
oleate.

References

T. Yamaguchi, Appl. Catal. 61, (1990), 1.

K. Arata, Adv. Catal. 37, (1990), 165.

J. R. Sohn and H. W. Kim, J. Mol. Catal. 52, (1989), 361.

L. Kustov, V. B. Kazansky, F. Figueras, and D. Tichit, J. Catal. 150, (1994), 143.

M. Hino, and K. Arata, J. Chem. Soc., Chem. Comm. (1979), 1148.

J. R. Sohn, H. J. Jang, M. Y. Park, E. H. Park, and S. E. Park, J. Mol. Catal. 93, (1994), 149.

J. R. Sohn, H. W. Kim, and J. T. Kim, J. Mol. Catal. 41, (1987), 375.

M. Hino, S. Kobayashi, and K. Arata, J. Am. Chem. Soc. 101, (1979), 6439.

K. Tanabe, in "Heterogeneous Catalysis" (B. L. Shapiro, Ed.), p. 71. Texas A&M Univ. Press
College Station, TX, 1984.

M. S. Scurrell, Appl. Catal. 34, (1987), 109.

M. Hino, and K. Arata, J. Chem. Soc., Chem. Commun. (1985), 112.

G. A. Olah, G. K. Prakash, and J. Sommer, "Super Acids." Wiley Interscience, New York,
1985, Chapter 5, pp. 243-344.

J. C. Yori, J. C. Luy, and J. M. Parera, Catal. Today 5, (1989), 493.

J. R. Sohn, and H. J. Kim, J. Catal. 101, (1986), 428.

H. Haerudin, S. Bertel, R. Kramer, J Chemical Society, Faraday Trans, 10, 94(1998), 1481.

H. Hirashima, H. Imai, V. Balek, J. Non-Crystalline Solids, 285 (2001), 96.

S. J. Teichner, in Aerogels, ed. J. Fricke. P. 22, Springer, Berlin, (1986)

I.M. K. Ismail and P. Pfeifer, Langmuir, 10, (1994), 1532.

A. Kurosaki, and S. Okazaki, Nippon Kagaku Kaishi 12, (1976), 1816.

S. Tursiloadi, Y. Yamanaka, H. Hirashima, J. Sol-Gel Sci. & Techn., , DOI 10.1007/s10971-
006-7849-1, 2006. , DOI 10.1007/s10971-006-7849-1, 2006.

J. R. Sohn, H. J. Kim, J. Catal. 101, (1986), 428.

Hans, J. B.; Johann, R.; Klemens, S.; Andreas, L., Ind. Eng. Chem. Res, 1994, 33, 21-25.

J. A. Laksmono, Y. Irawan, Wuryaningsih SR, E. Rijanto, Prosiding Seminar Nasional
Fundamental dan Aplikasi Teknik Kimia, Surabaya 7 – 8 Desember 2004, ISSN: 1410-5667.

Levenspiel, Octave, Chemical Reaction Engineering, Department of Chemical Engineering,
Oregon State University, John Willey & Sons, New York, 1972, pp. 10 – 30.