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Preparation of Nano Particles Sulfated Titania Catalyst Aerogel for Synthesis of Glycerol Mono Oleate (Gmo)

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Abstract: Catalysts nanoparticle sulfated titania aerogel have been prepared through one-step synthesis by the sol-gel method using sulfuric acid as catalyst followed by the one-step CO_2 supercritical extraction. The catalysts were tested in reaction of oleic acid with glycerol to produce glycerol mono oleate (GMO). Thermal evolution of the gels was evaluated by TGA-DTA, N_2 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 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 aerogels calcined at 500, 700 and 750°C have similar activities for synthesis of glycerol mono oleate surfactant. However, the activity of the aerogel calcined at 600°C is low. At 500°C, a relatively large amount of sulfate remains, and the aerogel has high activity.

Keywords: Nanoparticle sulfated titania, one-step CO_2 supercritical extraction, glycerol mono oleate.

I. Introduction

A catalyst has an important role in the chemical reaction. One type of catalyst is that widely used is the catalyst in the esterification process. Sulfated titania as solid acid catalyst is one of the modified titania gel products by reacting titania gel with sulfuric acid. Anatase titania has attracted much attention for its wide applications as key material in photocatalyst,[1] solar cells,[2] gas sensors[3] and electrochromic devices.[4] The acid strengths of sulfated titania anatase are high. New types of nonzeolitic 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.[5-12] 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.[13-19] Recently, considerable research attention has been directed towards several sulfated metal oxide systems.[20-26] 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 $-16.04 < H_0 < -14.52$,[6] 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 $55 m^2/g$,[27] and the poor stability of anatase at high temperatures, stable only below 500°C. [28]

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.[29]

In this work, the catalytic activities of resulting materials were evaluated for the esterification of oleic acid with glycerol to produce glycerol mono oleate. Palm oil in Indonesia is the largest plantation that spreads throughout the province. Indonesia is currently the world's largest producer of palm oil, with an area of 11.4 million ha. Indonesia's palm oil production in 2015 reached 31.9 million tons. [30] Most of Indonesia's palm oil production is still in the form of CPO (crude palm oil), this causes the added value of Indonesian palm oil is still low. One of the efforts undertaken to improve oil palm based agribusiness is to increase the added value of palm oil such as producing derivative products of palm oil.

One type of surfactant is a Glycerol mono oleate(GMO). GMO is a synthetic compound that is considered a monoglyceride. The petitioned purpose is for use as a defoamer, but the substance has a number of food applications, as well as application as an excipient in pharmaceutical products. The structure of glycerol mono oleate (GMO). The activity and selectivity of catalysts were compared by varying calcination temperature.

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II. Methodology

Materials

The materials used in this study were titanium tetra-n-butoxide (TNB), $Ti(n\text{-}OC_4H_9)_4$, aquadest, sodium hydroxide (NaOH), sulfuric acid (H_2SO_4) 96%, 70% ethanol, CO_2 and hydrogen.

Material Preparation

Titania sol-gel synthesis has been developed from inorganic precursors and from metal organic Ti(OR)4.[31] The sulfated-TiO_2 wet gel was prepared by hydrolysis of titanium tetra-n-butoxide (TNB), $Ti(n\text{-}OC_4H_9)_4$, 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 was completely gelled in 24h after addition of the catalyst. The un-sulfated-TiO_2 wet gel was prepared in the same condition using HNO_3 as catalyst for hydrolysis. The solution was completely gelled in 2 min after addition of the catalyst. 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. Schematic equipment (Supercritical Fluid Extraction System, Newport Scientific Inc.) as shown in Figure 1.

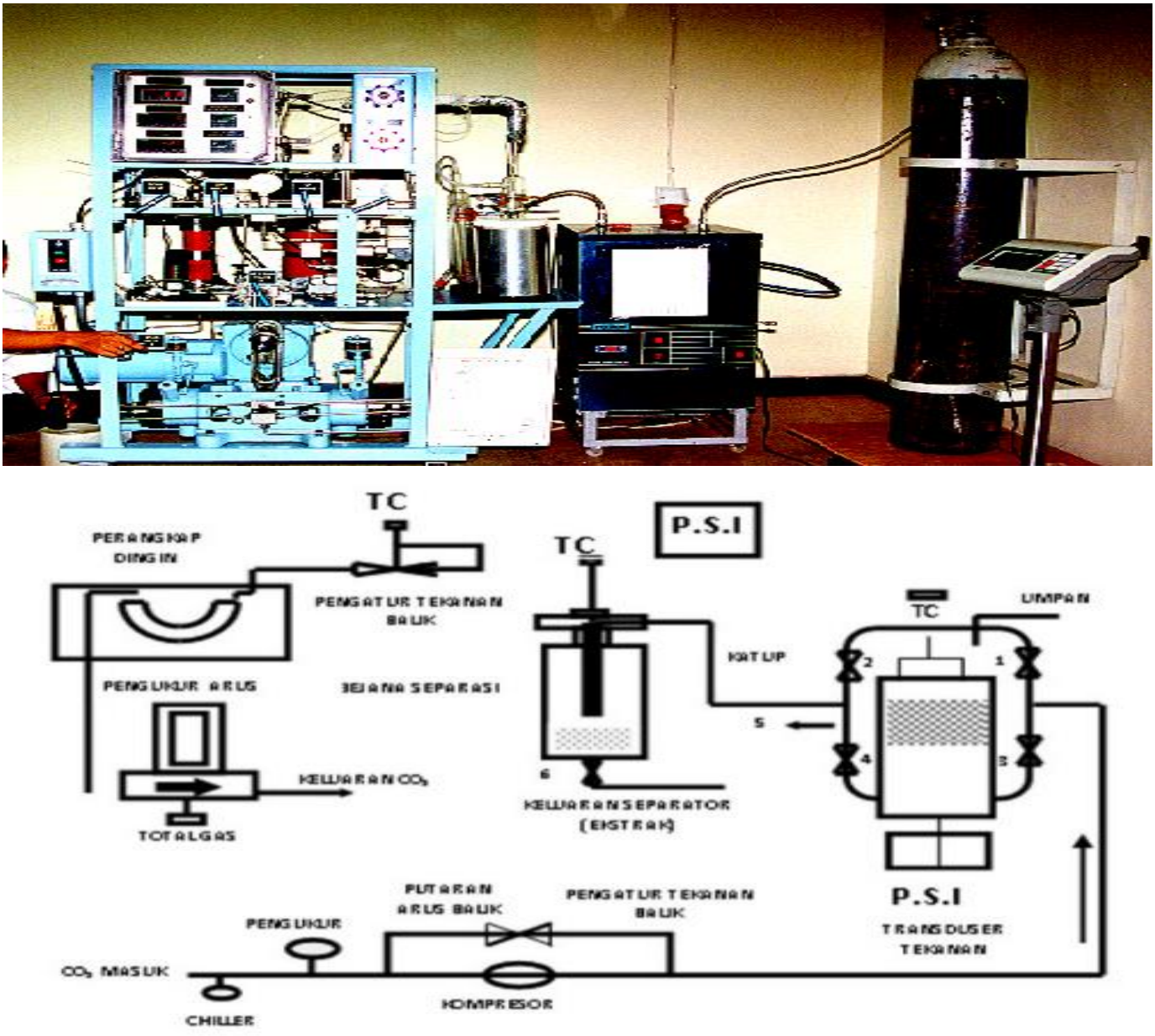

Fig.1. Supercritical Fluid Extraction System, Newport Scientific Inc.

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Changes in the nanostructure of the aerogel during heating were evaluated using thermo gravimetric and differential thermal analyses (TG-DTA, Seiko Exstar 6000 TG/DTA 6200 system) and N_2 adsorption measurements (Quantachrome, Autosorb). TG-DTA measurements were carried out under airflow of 300 ml min^{-1}, with a heating rate of 10°C 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 using N_2 adsorption-desorption curves.[32]

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 extracted 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 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}.

The catalytic activity of sulfated titania as-prepared and after calcination at various temperature, were evaluated for the reaction of oleic acid with glycerol to produce glycerol-mono-oleate when the molar ratio of oleic acid and glycerol was 1:1. The operational temperature was 180°C. 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 (yield).

III. Results and Discussion

Catalyst characterization

Gelling time of sulfated titania 24 h is much longer than that of un-sulfated titania e.g. 2 minutes. This showed that by using sulfuric acid as the catalyst for hydrolysis, the ion sulfate was coordinated to Ti^{4+} and formed bidentate sulfate (steric hindrance factor),[19] and then obstructed the reaction of formation polymerization of gel. The specific surface area of the sulfated and un-sulfated titania aerogel (Fig. 7a) 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.[33] 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.

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 100°C, a sharp exothermic peak and a weight loss about 10% at 240°C were observed. A broad and small exothermic peak at 400 °C and a small exothermic peak at 500°C accompanied with a gradual weight loss were observed. The total weight loss at temperatures up to 750°C was about 40%, and practically no more weight loss was observed at temperatures higher than 750°C. For the un-sulfated aerogel (Fig. 2b), weight loss about 5% was observed around 80°C. In the temperature range between 150 and 400°C, several small exothermic peaks and a gradual weight loss about 10% were observed. Beyond 400°C, the un-sulfated aerogel practically lose no more weight.

Solvent and other organic residue in the un-sulfated aerogel can be eliminated at temperatures up to 400°C (Fig. 2b). The first two weight losses observed for the sulfated aerogel, about 100°C accompanied with a small endothermic peak and up to 250°C accompanied with a strong exothermic peak, can be attributed to the evaporation and combustion of the solvent ethanol and sulfuric acid residue (Fig. 2a).

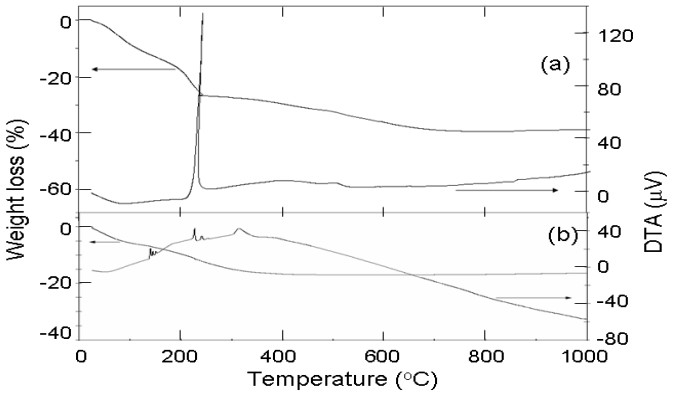

Fig. 2 TG-DTA profile of (a) sulfated titania aerogel and (b) un-sulfated aerogel.

Fig. 3. shows the FT-IR spectra of the sulfated gel as-extracted, calcined at 500, 600, 700 and 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}.[5, 34] The former is attributed to the stretching frequency of S=O and the latter

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bands are the characteristic frequencies of SO_4^{2-}.[5, 35] The as-extracted sample shows the presence of the absorption bands in the range from 1250 to 900 cm^{-1}, 1250, 1128, 1058, and 900 cm^{-1}, and strong peaks at 1635 cm^{-1} and at 1461cm^{-1}, attributed to the characteristic frequencies of SO_4^{2-}, and stretching of -OH and vibration of -C-H, respectively. [5] 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 400-600 cm^{-1} attributed to metal-oxygen bonds of Ti-O was found. [36]

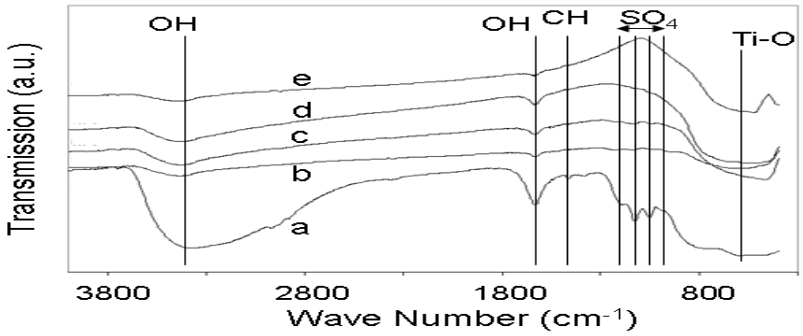

Fig. 3. IR absorption spectra of sulfated titania aerogel after calcination at various temperatures (a) as-prepared, (b) 500ºC, (c) 600ºC, (d) 700ºC, and (e) 800ºC

The X-ray powder diffraction pattern for the sulfated titania aerogel calcined at 500ºC shows the diffraction peaks of anatase (Fig. 4b). The anatase structure was stable after calcination up to 700ºC (Fig. 4d). After calcination at 800ºC, the diffraction peaks of anatase disappeared (Fig. 4e).[5] The wide peaks that appear at 2h = 25, 37, 47, 55, and 62_ are corresponded to the pure anatase crystalline phase.[37] Anatase is the most stable form by 8-12 KJ mol^{-1},[38] and can be converted to rutile by heating up to temperatures ~ 700ºC.[39]

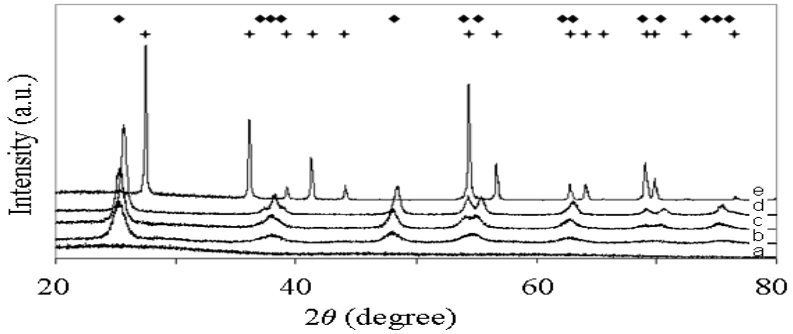

Fig. 4 XRD patterns of sulfated titania aerogel; (a) as-extracted, (b)500ºC, (c)600ºC, (d)700ºCand (e) 800oC. ◆ ; anatase ✦; rutile.

After calcinations at 600ºC, the small diffraction peaks of rutile were found (Fig. 5c). After calcination at 700ºC, the anatase peaks disappeared (Fig. 5d).[5] Therefore, anatase is obtained in processes under kinetic control, whereas processes involving Ostwald riping lead to the equilibrium phase, i.e., rutile.[40]

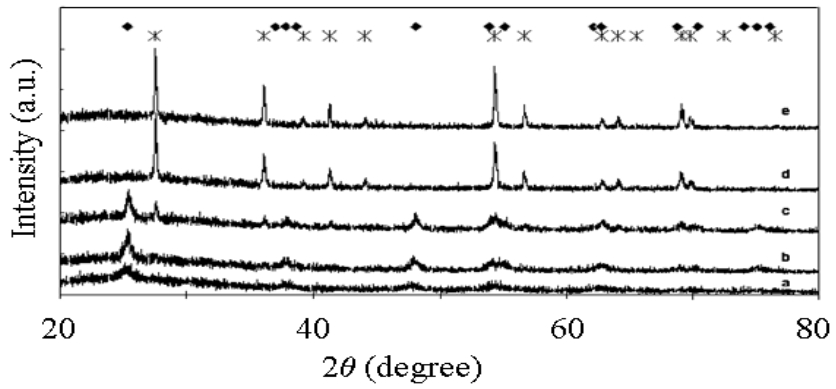

Fig.5 XRD patterns of un-sulfated titania aerogel; (a) as-extracted, (b) 500ºC, (c) 600ºC, (d) 700ºC and (e) 800ºC.; anatase *; rutile

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The X-ray diffraction peaks of anatase were found for the un-sulfated titania aerogel as-extracted (Fig. 5a). In fact, crystallization is highly influenced by the hydrolysis condition.[41] The anatase structure was stable after calcination at temperatures up to 500°C (Fig. 5b).

Figs. 6 show the TEM images and electron diffraction patterns of sulfated and un-sulfated TiO_2 aerogels as-extracted respectively. The as-extracted sulfated titania aerogel is in aggregate form and amorphous. For the as-extracted un-sulfated titania aerogel, many small crystalline particles were observed. The electron diffraction pattern also showed crystals with d = 0.362nm. The particle size of the un-sulfated TiO_2 aerogel as-extracted was ca. 5nm in diameter.

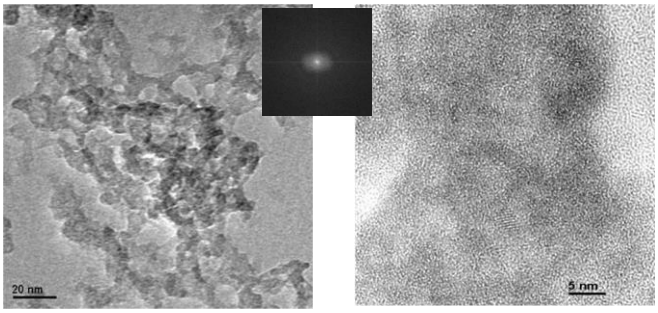
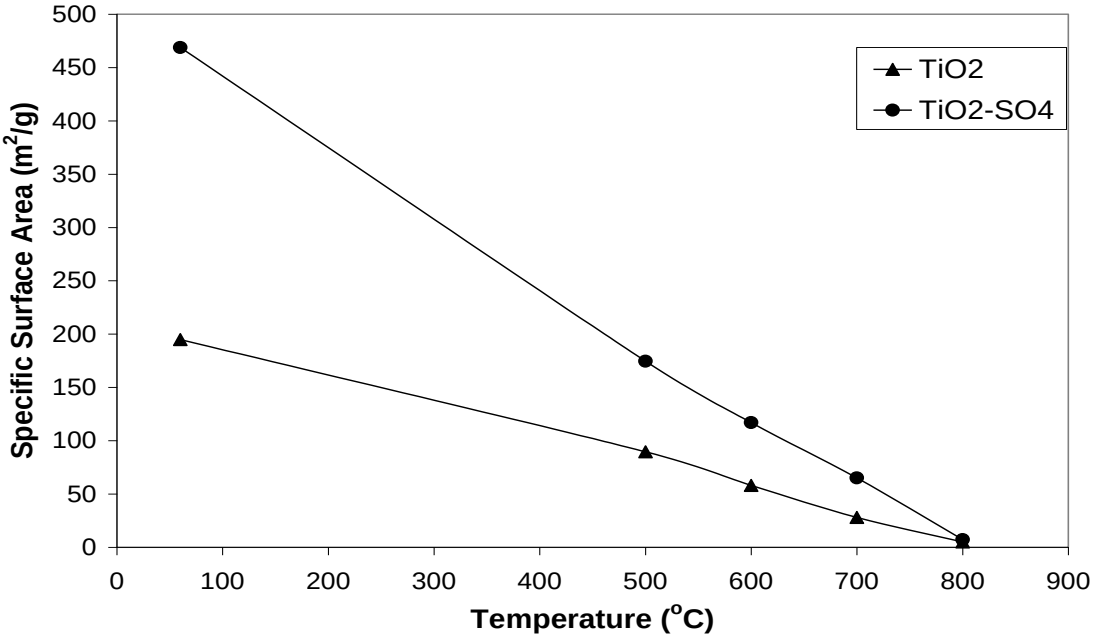


Fig.6 TEM image and electron diffraction pattern of (a) sulfated and (b) un-sulfated titania aerogel as-extracted.

Fig. 7 a,b,c show 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^2g^1, 11.9 nm and 1.60 cm^3g^{-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^2g^{-1} and 0.55 cm^3g^{-1}, respectively, more than two and three times, respectively (Fig. 7 a,b). After calcination at 500°C, the specific surface area and the pore volume of the sulfated titania, about 175 m^2g^{-1} and 0.94 cm^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 117 m^2g^{-1} and 0.74 cm^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 65 m^2g^{-1} and 0.4 cm^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 (Fig. 7 a,b). 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 (Fig. 7c).



(a)

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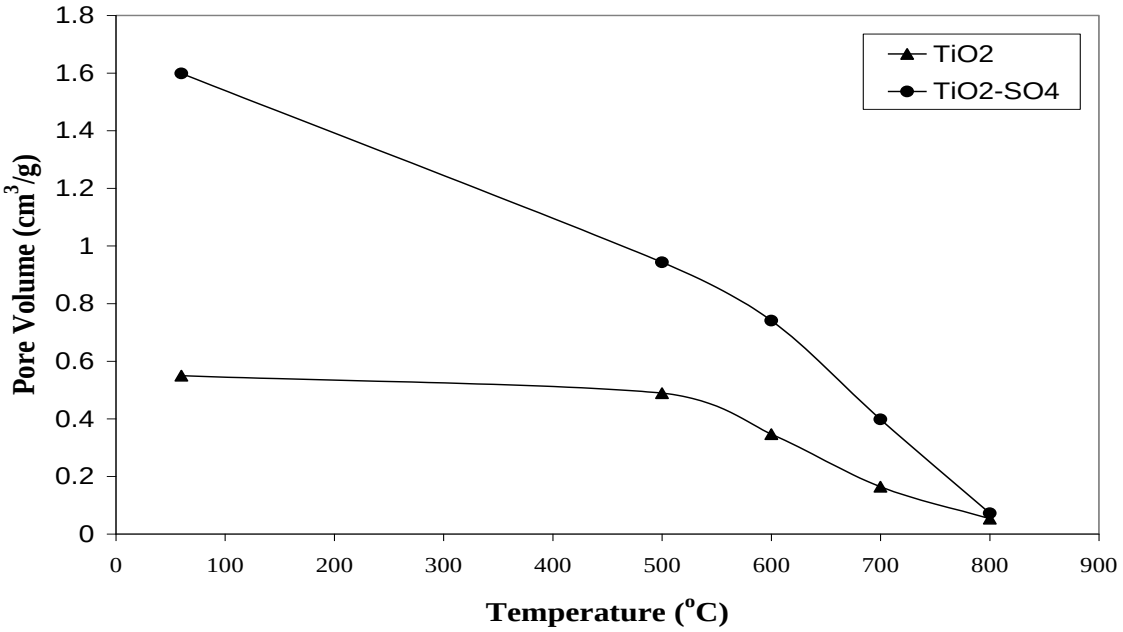
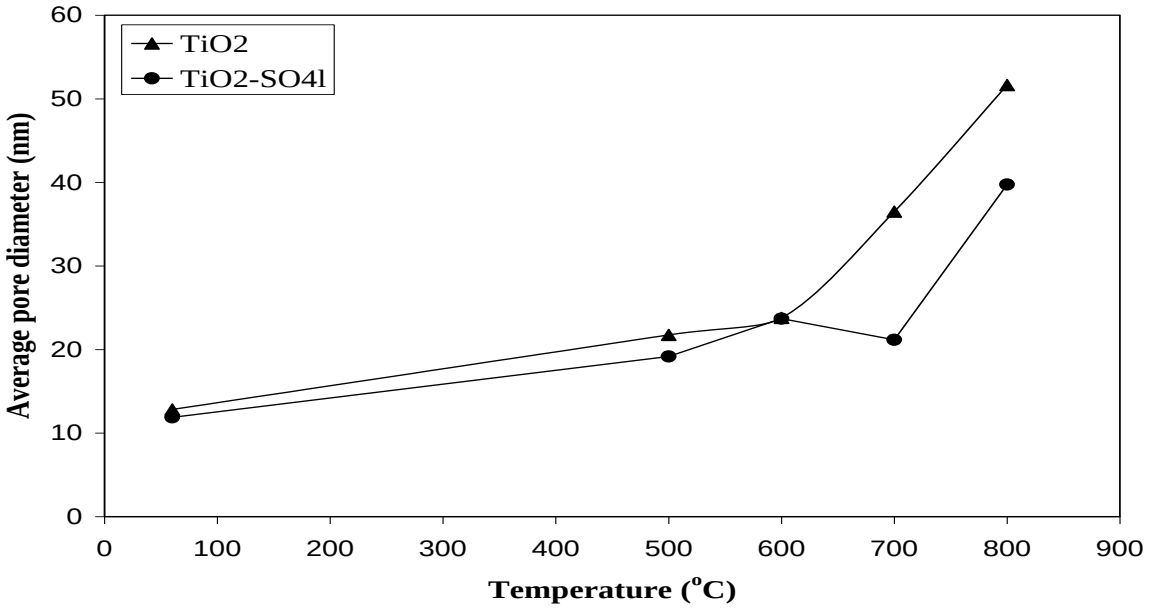


(b)



(c)

Fig. 7. Effect temperatures calcination: (a) on surface specific area; (b)pore volume ;(c) average pore size of sulfated titania and un-sulfated titania aerogel.

Catalysts activities

The effect of activation temperature of the sulfated titania on the catalytic activity for the reaction of oleic acid ($C_{18}H_{34}O_2$) with glycerol ($C_3H_8O_3$) to produce glycerol mono oleate.[5] Oleic acid ($CH_3(CH_2)_7CHCH(CH_2)_7COOH$) react readily with glycerol ($CH_2OHCHOHCH_2OH$) in the presence of catalytic amount of sulfated titania acids to yield compounds called Glycerol mono oleate (GMO)($CH_3(CH_2)_7CHCH(CH_2)_7COO\ CH_2OHCHOHCH_2$).

$$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$$

where R is $CH_3(CH_2)_7CHCH(CH_2)_7$and R' is $CH_2OHCHOHCH_2$. The as-prepared sulfated TiO_2 aerogel shows the high activity. The calcined sample at 800ºC shows the lowest activity than the others.

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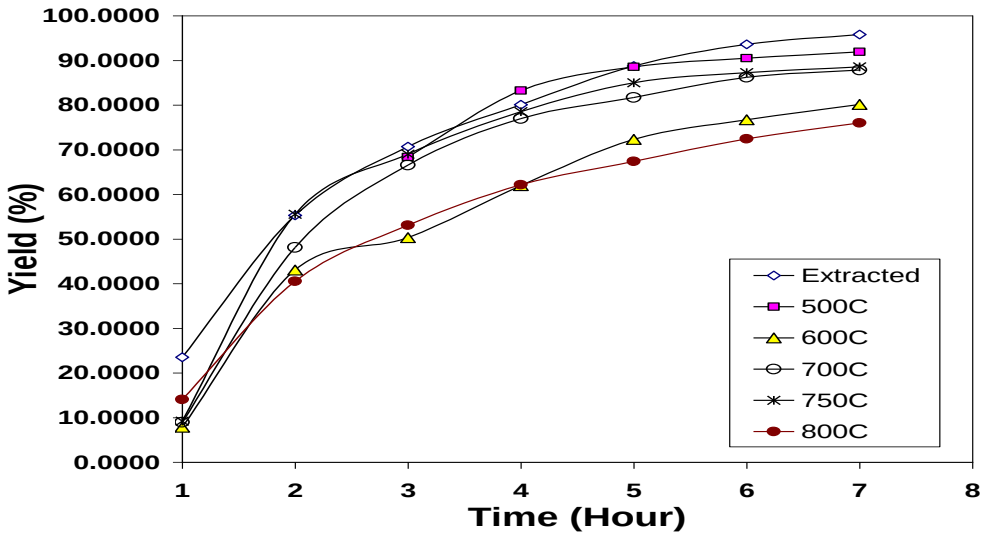

Fig.8.Effect of activation temperatures of the sulfated titania on the catalytic activity on production of glycerol mono oleate.

Glycerol monooleate (GMO) synthesized via esterification involves reaction between glycerol and oleic acid, the esterification reaction is intrinsically slow, requiring the use of catalyst to decrease the activation energy. [42] The catalyst based on zeolites with many modification.[42,43] Using Mordenite natural zeolite, catalyst loading of 2 wt%, resulted GMO conversion of 75.09 %.[43] Zirconia-Silica and commercial acid catalysts used for esterification of glycerol with oleic acid resulted conversion of GMO 59.4 %.[44] Esterification reaction of oleic acid and glycerol produced of GMO using H-ZSM-5 catalyst and microwave as a heat source, 1% catalyst weight, ratio of reactant 2:1, reaction time of 50 minutes, and temperature of 160 ^{o}C resulted a yield value of 92,02 %.[45] Natural zeolite used as catalyst for glycerolysis at temperature of 220 ^{o}C resulted the conversion value of 95 %.[46]

The sulfated titania catalysts with several treatment used for catalytic of the conversion of GMO as shown in Figure 8. The activities of catalysts were changed by changing of heat treatment. The specific area and pore volume were decreased drastically after calcination of 500 ^{o}C and nearly zero in the heat treatmecayalyst and microvant of 800 ^{o}C (Fig.7 a,b), but average pore diameters were increased by increasing calcination temperature (Fig.7c). The catalysts activity was not inherent with the decreasing of specific area and pore volume. Catalysts calcined at 750 ^{o}C has hgher yield than catalysts at 600 and 700 ^{o}C. Eventhough catalysts calcined at 600 and 700 have higher surface area and pore volume. The extracted catalysts have higher yield, followed by 500 ^{o}C and 700 ^{o}C heat treatment. The lower yield laid on the 600 and 800 ^{o}C heat treatment.

After calcination at 500 ^{o}C, the most sulfates in the titania particles is expelled onto the surface of titania nanoparticles with crystallization (Fig. 4b). During this process, some sulfate is lost (Fig. 2a) and some dehydroxylation occurs. The majority of the sulfate is expelled onto the surface. Now, sulfate is on the surface, and the sulfate transformed into an active state. There are showed that calcination at 500 ^{o}C gave higher yield. The structural stability of the sulfated aerogel is due to the stability of anatase phase. The grain growth and phase transformation of anatase are restrained with the surface sulfate, Ti_2SO_4.[6,19]

The TG profile (Fig. 2a) shows that the decomposition of sulfate phase in the TiO_2 continues up to 750 ^{o}C. As long as sulfate was present, the phase transformation from anatase to rutile is retarded. And, when the entire sulfate is removed after calcinations at 800 ^{o}C, the aerogel converted to the rutile phase. After calcination at 800 ^{o}C, the absorption bands 1250, 1128, 1058, and 900 cm^{-1} attributed to the sulfate are disappeared. The aerogel calcined at 800 ^{o}C shows the lowest activity for synthesis of glycerol mono oleate surfactant because that the entire sulfate is removed.

IV. Conclusions

Sulfated titania (TiO_2-SO_4^{2-}) aerogel has been prepared by one-step synthesis through the sol-gel method using sulfuric acid as hydrolysis catalyst followed by the one-step CO_2 supercritical extraction. The introduction of sulfuric acid into the titania aerogel results in the formation of sulfate phase, bridged bidentate Ti_2SO_4. Sulfate ions can be anchored to anatase, because they have short O-O atomic bond lengths that are slightly larger than the largest O-O bond length of the sulfate ion. The specific sulfate phase in the sulfated TiO_2 aerogel is stable up to 700^{o}C, and the decomposition temperature is much higher than that of the sulfated TiO_2 gel prepared by impregnation. It makes them attractive from the catalytic point of view. The presence of sulfate in amorphous titania prevents the crystallization of anatase at low temperature during supercritical extraction. The porous structure of the sulfated aerogel is thermally stable in comparison with the un-sulfated aerogel. The sulfate phase, Ti_2SO_4, restrains the crystallization and the grain growth of anatase, and retards the phase transformation from anatase to rutile. The aerogels calcined at 500, 700 and 750^{o}C have similar activities for synthesis of glycerol mono oleate surfactant. However, the activity of the aerogel calcined at 600^{o}C is low. At 500^{o}C, a relatively large amount of sulfate remains and the aerogel has high activity.

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