

Acid-catalyzed regeneration of fatty-acid-adsorbed γ -alumina via transesterification with methanol

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Abstract—Fatty-acid-adsorbed γ -alumina was regenerated via transesterification using methanol with sulfuric acid as a catalyst. The fatty acids adsorbed on γ -alumina were converted to fatty acid methyl esters (FAME) and desorbed from the γ -alumina during the acid-catalyzed methanol regeneration process. A series of experiments studied the effect of the operating parameters (temperature, amount of sulfuric acid (wt%), methanol-solution-to- γ -alumina weight ratio, and regeneration time) on the acid-catalyzed methanol regeneration process. The chemically adsorbed fatty acids were desorbed effectively above 100 °C when the amount of sulfuric acid was 3 wt%, the methanol-solution-to- γ -alumina weight ratio was higher than 5 : 1, and the regeneration time was longer than 30 min. This new approach provides an ecofriendly process that operates at much lower temperatures than other methods of regeneration (thermal and supercritical methanol) while producing a renewable fuel.

Keywords: Desorption, γ -Alumina, Fatty Acid, Regeneration, Transesterification

INTRODUCTION

Activated alumina has a wide range of applications. Its high surface area and many tunneled pores mean that it can be used as a desiccant, fluoride filter, or adsorbent. Activated alumina adsorbs moisture from the air, converting the surface functional groups of alumina to hydroxyl groups. The carboxylic acids can be esterified by the hydroxyl groups on the alumina surface, which has a higher affinity for carboxylic acids than other functional groups [1,2]. Therefore, the selective adsorption of carboxylic acids using activated alumina could be used in the deacidification field.

Free fatty acids (FFA) in vegetable oils are considered to be the main causes of oil rancidity and should not be present in high concentrations during biodiesel production because they consume the base catalyst. Thus, deacidification is a crucial refining process that has been extensively studied in vegetable oil and biodiesel refining. Chemical, physical, and micelle-based deacidification are conventional industrial processes [3]. Among such processes, chemical deacidification, which involves neutralization with an alkali, is the most well-known. However, the loss of neutral oil during the washing step, arising from the saponification of oil, is a major drawback of chemical deacidification. Thus, new approaches, such as biological deacidification [4,5], chemical re-esterification [6], solvent extraction [7-9], supercritical fluid extraction [10,11], and membrane technology [12,13], are required to overcome the drawbacks of the conventional processes.

Deacidification using activated alumina as an adsorbent could overcome the drawbacks of conventional processes. The deacidifi-

cation of vegetable oils using a chromatographic process, which uses activated alumina as the stationary phase at room temperature, has been proposed [14]. This process has several advantages, including the minimization of the loss of neutral oil and prevention of the emulsion problem. The spent alumina should be regenerated in a cost-effective way. However, the conventional thermal regeneration process, which usually requires a high operating temperature, consumes a significant amount of energy because of the chemisorption of the fatty acids. In previous reports, a temperature of 550 °C or higher was required for the thermal regeneration of palmitic-acid-adsorbed γ -alumina thermally. In order to reduce the regeneration temperature, a novel regeneration method for palmitic-acid-adsorbed γ -alumina using supercritical methanol was introduced. The chemically adsorbed palmitic acid is converted to palmitic acid methyl ester via transesterification with supercritical methanol and is desorbed from the γ -alumina. The optimum conditions of supercritical methanol regeneration are 300 °C, 300 bar, a methanol-to- γ -alumina weight ratio of 75 : 1, and a reaction time of 15 min. The operating temperature of the developed method, which produces biodiesel in an eco-friendly manner, is much lower than that of the thermal regeneration method [15].

Transesterification, which refers to the reaction of exchanging the organic R group of an ester with the R' group of an alcohol, has been applied in various fields such as the synthesis of polyesters and the production of biodiesel. Biodiesel is an attractive renewable fuel to replace fossil fuels. To produce biodiesel, triglycerides (TG), which are the main components of vegetable oils, are converted to long-chain fatty acid alkyl esters by reaction with alcohols, usually methanol or ethanol, but methanol is preferred for its low cost and fast reaction. Because the transesterification reaction is reversible, excess alcohol is used to shift the equilibrium toward the transesterified product. In addition, a strong acid or base is often used as a homo-

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geneous catalyst to increase the reaction rate. Common production conditions of biodiesel are 60-100 °C, 30-120 min, a molar ratio of oil/methanol 1 : 6 to 1 : 30, and 0.5-2.5 wt% catalyst. It has been reported that the alkali-catalyzed transesterification reaction is faster than acid-catalyzed reaction [16]. In general, the acid-catalyzed reaction requires higher operating temperatures and longer reaction times than the alkali-catalyzed reaction [16].

We studied the regeneration of the fatty-acid-adsorbed γ -alumina through transesterification using methanol with sulfuric acid as a catalyst. The regenerated γ -alumina was analyzed by thermal gravimetric analysis (TGA), and Fourier transform infrared (FT-IR) spectroscopy, and the reaction product was analyzed qualitatively and quantitatively using gas chromatography/mass spectroscopy (GC/MS) to study the mechanism of regeneration. The experiments were carried out at several temperatures, amounts of sulfuric acid (wt%), weight ratios of methanol-solution-to- γ -alumina, and regeneration times to determine the optimum conditions for the regeneration of fatty-acid-adsorbed γ -alumina. Several adsorption-desorption cycles were performed to study the maintenance of the adsorption capacity of the regenerated γ -alumina. After acid-catalyzed methanol regeneration, the crystal structure and surface area of the regenerated γ -alumina catalyst were studied using X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) analyses for comparison with the other methods (thermal regeneration method and supercritical methanol regeneration method).

EXPERIMENTAL

1. Preparation of Palmitic-acid-adsorbed γ -Alumina

The model fatty acid was palmitic acid (C16 fatty acid), which was obtained from Sigma-Aldrich. Extrude-type γ -alumina (AL-3992 1/8, Engelhard), which was selected as the adsorbent was ground to particles of with diameters of 45 and 150 μm to decrease external and internal diffusion resistance. As a result, the reaction time and amount of sulfuric acid required to achieve the desired regeneration would be decreased due to the small particle size of γ -alumina. The adsorption process occurred in a closed glass bottle containing 400 mL of dichloromethane, 1 g of palmitic acid, and 2 g of γ -alumina. A magnetic stirrer was used to stir the palmitic acid solution with γ -alumina for 24 h at near room temperature. After 24 h, the γ -alumina was carefully separated from the palmitic acid solution and washed with neat dichloromethane using a centrifuge. The washed γ -alumina was dried for 2 h in a vacuum oven at 40 °C and a pressure of 600 mmHg to remove the residual dichloromethane. The amount of adsorbed palmitic acid on γ -alumina was calculated by titration of the separated solution.

2. Regeneration of Palmitic-acid-adsorbed γ -Alumina Using Methanol with/without Sulfuric Acid

A 23-mL batch type reactor made of stainless steel (SUS316) was used to regenerate the palmitic-acid-adsorbed γ -alumina. The reactor was heated in an oil bath (COB-22, Chosun Instruments) and fitted with an electric shaker. The palmitic-acid-adsorbed γ -alumina and methanol (J.T. Baker) with varying concentrations of sulfuric acid were loaded into the reactor under the selected experimental conditions. After the methanol solution (methanol with sulfuric acid) treatment, the regenerated γ -alumina at the bottom of batch

type reactor was carefully filtered out and separated from the methanol solution. The separated γ -alumina was washed with neat methanol to remove the sulfuric acid and reaction product. The washed γ -alumina was dried under vacuum (600 mmHg) at 50 °C for 2 h. TGA, BET, and XRD were used to analyze the regenerated γ -alumina. The evaporation of the methanol in the filtrate was conducted using a vacuum oven (600 mmHg) at 40 °C for 3 h. The dried filtrate was dissolved in *n*-heptane and mixed with deionized water to separate reaction product and sulfuric acid. After rapid phase separation, the organic solvent phase was analyzed using GC/MS. To investigate the maintenance of adsorption capacity of γ -alumina, it was washed and repeatedly dried after methanol solution treatment.

3. Characterization

3-1. Thermal Gravimetric Analysis

TGA/DTG curves of γ -alumina samples were obtained using an SDT Q-600 V20.9 (TA Instruments, USA) instrument. At least 2 mg of sample was loaded into the instrument and heated at a rate of 10 °C min^{-1} to 600 °C under a nitrogen atmosphere.

3-2. Gas Chromatography

GC/MS was used to analyze the reaction products of acid-catalyzed methanol regeneration. The reaction products and internal standard (methyl heptadecanoate) were dissolved in *n*-heptane and injected into an Agilent 7890A instrument with a 5975C mass spectrometer for quantitative analysis. An HP-5ms (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 μm) column and a triple-axis HED-EM detector were used. The flow rate of the carrier gas (high-purity helium 99.9999%) was 1 mL min^{-1} , and the inlet (split mode, ratio 5 : 1) and the detector temperature were kept at 260 °C. The temperature of the oven was increased from 150 to 250 °C at a rate of 5 °C min^{-1} , which was maintained for 10 min. The temperature of the ionization source was constant at 230 °C, and the quadrupole temperature was maintained at 150 °C.

3-3. X-ray Diffraction

X-ray diffraction patterns of regenerated γ -alumina were obtained using a D-MAX-2500 PC (Rigaku, Japan) diffractometer. The scanning range was from 10° to 90° at a scan speed of 5° min^{-1} . The JCPDS reference pattern was used to identify X-ray pattern of regenerated γ -alumina.

3-4. Fourier Transform Infrared Spectrometry

The surface functional groups of γ -alumina samples were analyzed with a Nicolet 6700 (Thermo Scientific, USA). The scanned wavenumber range was from 4,000 to 650 cm^{-1} .

3-5. Brunauer-Emmett-Teller Surface Area

An ASAP 2020 device was used to obtain the N₂ adsorption/desorption isotherms of γ -alumina. The γ -alumina samples were degassed for 6 h at 473 K in a vacuum of less than 10⁻³ Torr before the measurement. The BET equation was used to calculate the specific surface area.

RESULTS AND DISCUSSION

1. Characterization of Raw γ -Alumina, Methanol-treated Raw γ -Alumina, and Methanol-solution-treated Raw γ -Alumina

Fig. 1 shows the TGA/DTG analysis of raw γ -alumina, methanol-treated raw γ -alumina, and methanol-solution-treated raw γ -alumina. The removal of physically adsorbed moisture caused weight losses

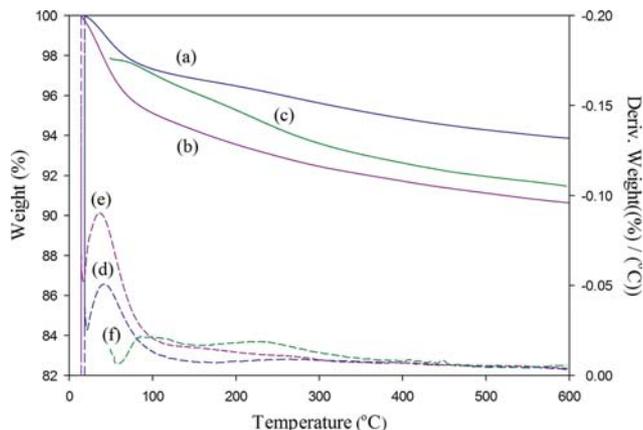


Fig. 1. TGA/DTG analysis of raw γ -alumina ((a) and (d)), methanol-treated raw γ -alumina ((b) and (e)), and methanol-solution-treated raw γ -alumina ((c) and (f)). (a) Weight loss of raw γ -alumina. (b) Weight loss of methanol-treated raw γ -alumina (100 °C). (c) Weight loss of methanol-solution-treated raw γ -alumina (100 °C). (d) Derivative weight loss of raw γ -alumina. (e) Derivative weight loss of methanol-treated raw γ -alumina (100 °C). (f) Derivative weight loss of methanol-solution-treated raw γ -alumina (100 °C).

from the raw γ -alumina, methanol-treated raw γ -alumina, and methanol-solution-treated raw γ -alumina of 2 to 4 wt% up to 100 °C, as shown in Fig. 1(a), (b), and (c). When the temperature exceeded 150 °C, the weight loss rates of γ -alumina decreased remarkably owing to the desorption of chemisorbed moisture in contrast to the weight loss rates of physically adsorbed moisture. The shapes of the TGA/DTG curves of raw γ -alumina, methanol-treated raw γ -alumina, and methanol-solution-treated raw γ -alumina were almost identical. These results demonstrate that neither methanol nor methanol solution treatment cause major changes in the TGA/DTG curves of raw γ -alumina.

2. Effect of Process Parameters on the Regeneration of Palmitic-acid-adsorbed γ -Alumina Using Methanol with/without Sulfuric Acid

2-1. Regeneration of Fatty-acid-adsorbed γ -Alumina without a Homogeneous Catalyst

The palmitic-acid-adsorbed γ -alumina showed the maximum

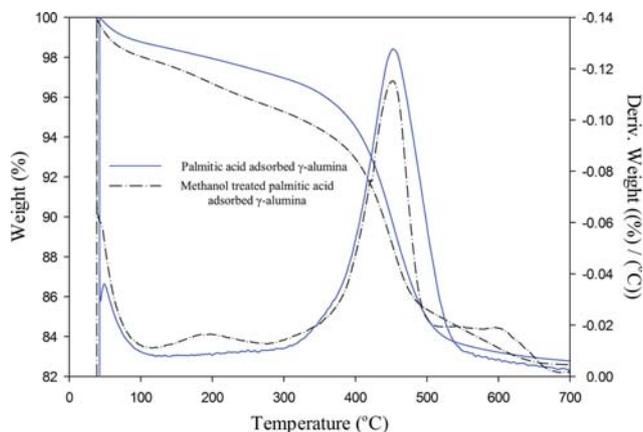


Fig. 2. TGA/DTG analysis of adsorbed palmitic acid on γ -alumina and methanol-treated palmitic-acid-adsorbed γ -alumina.

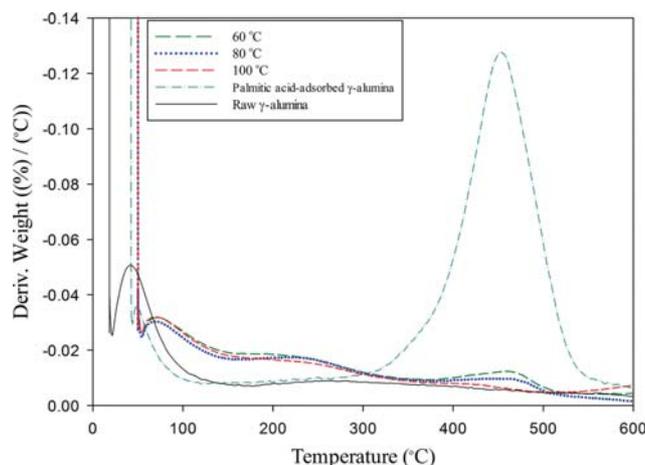


Fig. 3. Derivative weight loss curves of raw γ -alumina, palmitic-acid-adsorbed γ -alumina, and γ -alumina regenerated by a methanol solution at temperatures of 60, 80, and 100 °C.

rate of desorption of palmitic acid (0.1276 wt%/°C) at around 452 °C, which was attributed to the desorption of the chemisorbed palmitic acid on γ -alumina [15]. There was a minor transition in the TGA/DTG curve of methanol-treated palmitic-acid-adsorbed γ -alumina, which demonstrates that adsorbed palmitic acid was not desorbed without a homogeneous catalyst at 100 °C and regeneration time of 30 min, as shown in Fig. 2. Thus, sulfuric acid was added to regenerate the palmitic acid adsorbed γ -alumina effectively in the subsequent experiments.

2-2. Regeneration of Fatty-acid-adsorbed γ -Alumina with a Homogeneous Catalyst

2-2-1. Effect of Regeneration Temperature

Fig. 3 shows the TGA/DTG curves of regenerated γ -alumina at various regeneration temperatures. The experimental parameters, except regeneration temperature, were kept constant. The desorption data was analyzed based on the weight loss rate of the regenerated γ -alumina rather than the absolute weight loss, particularly the maximum weight loss rate of regenerated γ -alumina at around 450 °C. The derivative peak around 450 °C indicates the loss of adsorbed palmitic acid from the surface of γ -alumina. A tiny peak in the DTG curve of regenerated γ -alumina was observed around 450 °C, which indicates that the adsorbed palmitic acid was not removed completely at a regeneration temperature of 60-80 °C. On the other hand, the weight loss rate of regenerated γ -alumina at 100 °C is almost identical to the weight loss rate of raw γ -alumina. These results demonstrate that all the adsorbed palmitic acid was removed from the γ -alumina. Thus, a regeneration temperature of 100 °C was sufficient for the regeneration of palmitic-acid-adsorbed γ -alumina through transesterification using methanol with sulfuric acid as a catalyst.

2-2-2. Effect of the Methanol-solution-to- γ -alumina Weight Ratio with Different Amounts of Sulfuric Acid (wt%)

The methanol-solution-to- γ -alumina weight ratio is also an important operating parameter, as is the amount of sulfuric acid (wt%). Thus, experiments were carried out by varying the methanol-solution-to- γ -alumina weight ratio (2 : 1, 5 : 1, 10 : 1, 25 : 1, and 50 : 1) and the amount of sulfuric acid (1 and 3 wt%) while the other experimental parameters were kept constant.

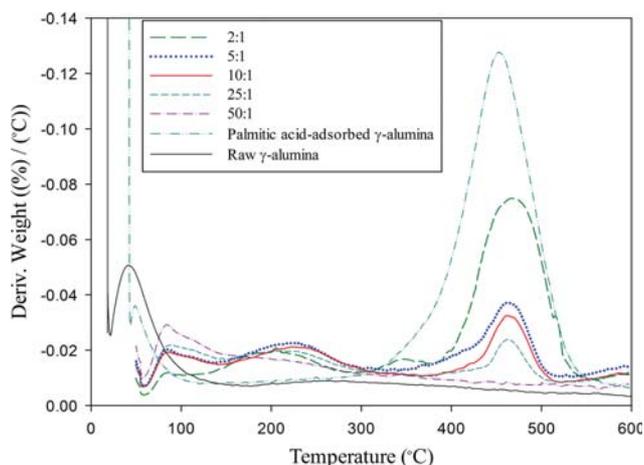


Fig. 4. Derivative weight loss curves of raw γ -alumina, palmitic-acid-adsorbed γ -alumina, and γ -alumina regenerated by a methanol solution (1 wt% sulfuric acid) with methanol-solution-to- γ -alumina weight ratios of 2 : 1, 5 : 1, 10 : 1, 25 : 1, and 50 : 1.

Figs. 4 and 5 show that the maximum weight loss rate of regenerated γ -alumina decreased gradually as the methanol-solution-to- γ -alumina weight ratio increased. The palmitic-acid-adsorbed γ -alumina was completely regenerated at a methanol-solution-to- γ -alumina weight ratio of 50 : 1 when the amount of sulfuric acid was 1 wt% in Fig. 4.

Almost identical results were obtained with a methanol-solution-to- γ -alumina weight ratio of 5 : 1 or higher when the amount of sulfuric acid was increased from 1 to 3 wt%, as shown in Fig. 5. It was possible to regenerate ten-times the amount of palmitic-acid-adsorbed γ -alumina when 3 wt% sulfuric acid was used. Thus, a large quantity of sulfuric acid (3 wt%) is effective in treating the palmitic-acid-adsorbed γ -alumina and a methanol-solution-to- γ -alumina weight ratio of 5 : 1 was sufficient for regeneration.

2-2-3. Effect of Regeneration Time

The TGA/DTG curves of regenerated γ -alumina treated with

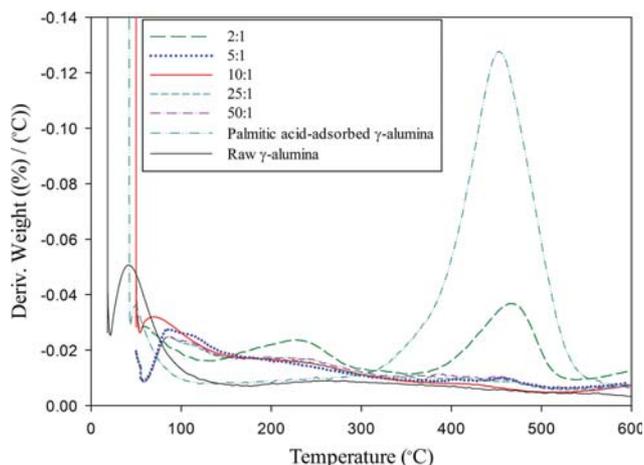


Fig. 5. Derivative weight loss curves of raw γ -alumina, palmitic-acid-adsorbed γ -alumina, and γ -alumina regenerated with a methanol solution (3 wt% sulfuric acid) and methanol-solution-to- γ -alumina weight ratios of 2 : 1, 5 : 1, 10 : 1, 25 : 1, and 50 : 1.

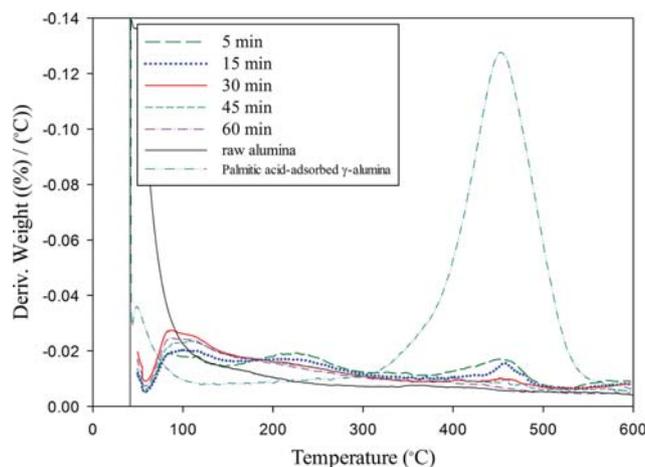


Fig. 6. Derivative weight loss curves of raw γ -alumina, palmitic-acid-adsorbed γ -alumina, and regenerated γ -alumina by a methanol solution with regeneration times of 5, 15, 30, 45, and 60 min.

methanol solution for various regeneration times (5, 15, 30, 45, and 60 min) are shown in Fig. 6. The other experimental parameters were kept constant at a temperature of 100 °C, 3.0 wt% sulfuric acid, and a methanol-solution-to- γ -alumina weight ratio of 5 : 1.

The maximum weight loss rate (0.1276 wt%/°C) of palmitic-acid-adsorbed γ -alumina decreased sharply to 0.01707 wt%/°C after 5 min of methanol solution treatment. These results indicate that most of the adsorbed palmitic acid had desorbed, although some palmitic acid remained on the γ -alumina. A slight decrease in the peak intensity around 450 °C was observed with increasing regeneration time. Identical repeated weight loss rates of the regenerated γ -alumina were obtained at regeneration times longer than 30 min, indicating that almost all of the adsorbed palmitic acid had been removed from γ -alumina after 30 min.

2-2-4. Maintenance of the Adsorption Capacity of γ -Alumina

The adsorption and desorption of γ -alumina were repeated to study the maintenance of the adsorption capacity of γ -alumina,

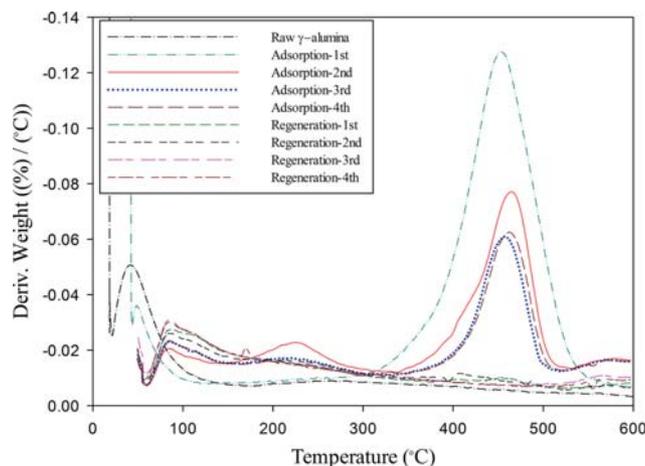


Fig. 7. Derivative weight loss curves of raw γ -alumina, palmitic-acid-adsorbed γ -alumina (1st, 2nd, 3rd, and 4th), and γ -alumina regenerated by methanol solution (1st, 2nd, 3rd, and 4th).

which was regenerated using a methanol solution. The adsorption of palmitic acid on γ -alumina was conducted as described in the Experimental section. The optimum conditions for acid-catalyzed methanol regeneration were used to regenerate the palmitic-acid-adsorbed γ -alumina (100 °C, 3 wt% of sulfuric acid, methanol-solution-to- γ -alumina weight ratio of 5:1, and a regeneration time of 30 min). The virgin γ -alumina showed the highest rate of weight loss and largest peak area around 450 °C, indicating that it has the largest adsorption capacity, as shown in Fig. 7. A gradual reduction in adsorption capacity was observed up to the third adsorption. This is attributed to partial conversion of the γ -alumina surface to aluminum sulfate, as detected by FT-IR analysis during methanol solution treatment. Almost identical results for the regenerated γ -alumina samples were obtained after acid-catalyzed methanol regeneration, indicating that palmitic acid adsorbed on γ -alumina was desorbed irrespective of the number of cycles.

3. Identifying the Surface Functional Group Change of γ -Alumina During Acid-catalyzed Methanol Regeneration

The γ -alumina samples were analyzed by FT-IR to obtain information about the surface functional groups. Figs. 8(a) and (b) show that the surface functional group of raw γ -alumina remained unchanged during neat methanol treatment at 100 °C. These results are in agreement with the TGA/DTG curves shown in Fig. 2. On the other hand, sulfate peaks (1,150-1,130 and 1,060 cm^{-1}) can be seen in Figs. 8(c) and (f), indicating that part of the surface of γ -alumina was converted to aluminum sulfate by sulfuric acid. In Fig. 8(d), there are methylene peaks (2,850-2,950 and 1,470 cm^{-1}) and a carbonyl peak around 1,500 cm^{-1} , which arise from the chemisorption of palmitic acid on γ -alumina [15]. Both the methylene and carbonyl peaks almost disappeared after acid-catalyzed methanol regeneration because of the desorption of palmitic acid from the surface of γ -alumina at 100 °C using 3 wt% sulfuric acid, a methanol-solution-to- γ -alumina weight ratio of 5:1, and a regeneration time of 30 min. The FT-IR patterns of the other regenerated γ -alumina were very similar. However, it was challenging to

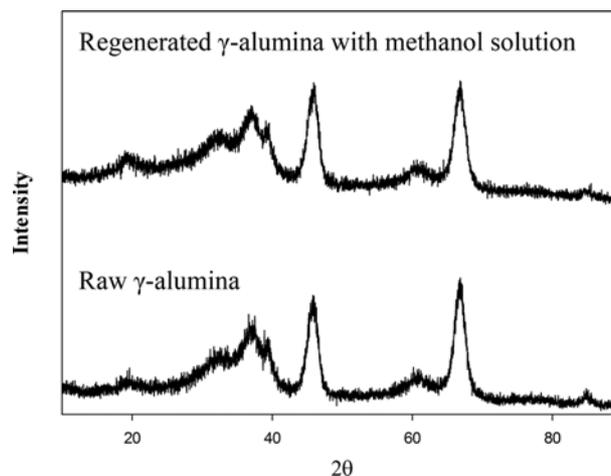


Fig. 9. XRD patterns of raw γ -alumina and regenerated γ -alumina using methanol solution (100 °C, 3 wt%).

identify the C-O peak (1,050-1,100 cm^{-1}), which was detected clearly after supercritical methanol treatment because the methylation of the surface functional groups (Al-O-Al to Al-O-CH₃ and Al-O) may not occur during acid-catalyzed methanol regeneration.

4. Identifying Changes in the Crystal Structure of γ -Alumina after Acid-catalyzed Methanol Regeneration

The regenerated γ -alumina was analyzed by XRD to identify changes to the crystal structure after methanol solution treatment. The XRD patterns of γ -alumina that had been regenerated at 100 °C using a methanol-solution-to- γ -alumina weight ratio of 5:1 and regeneration time of 30 min are presented in Fig. 9. Reflections corresponding to aluminum sulfate, whose presence is indicated by the IR patterns shown in Fig. 8, were not detected. These results demonstrate that conversion to aluminum sulfate is confined to the surface of the γ -alumina. Thus, the bulk crystal structure of γ -alumina was not modified except for part of the surface after acid-

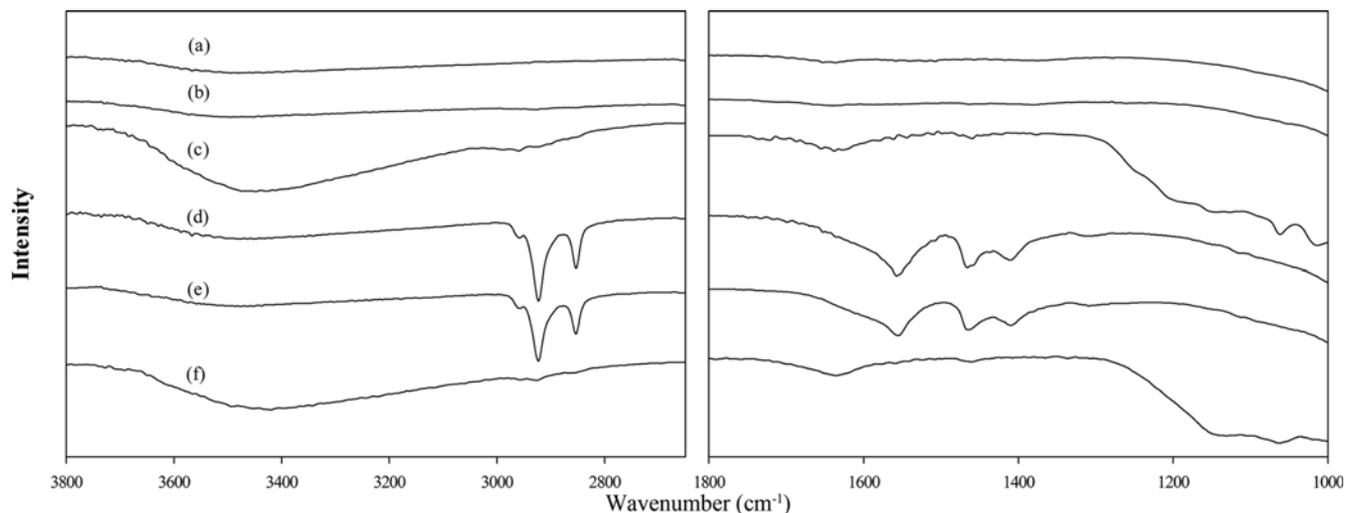
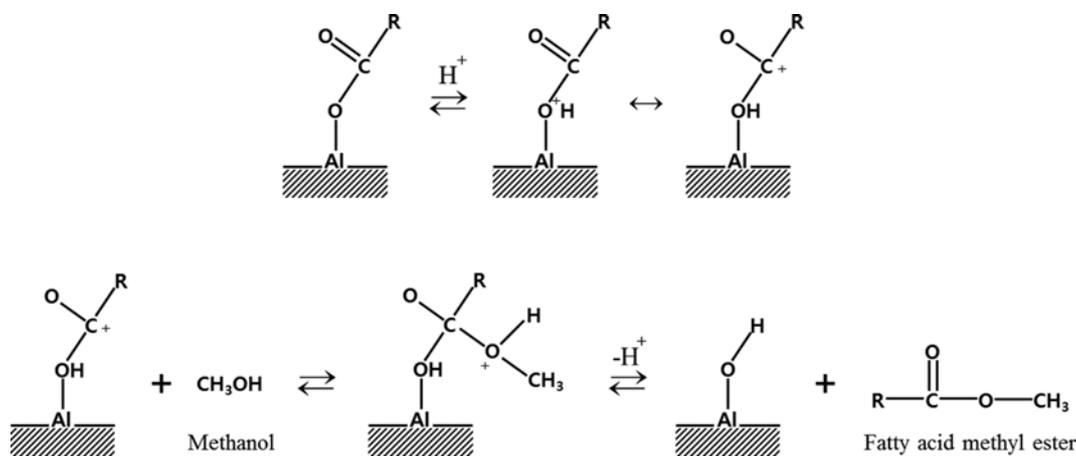


Fig. 8. FT-IR patterns of (a) raw γ -alumina, (b) methanol-treated raw γ -alumina (100 °C), (c) methanol-solution-treated raw γ -alumina (100 °C, 3 wt%), (d) palmitic-acid-adsorbed γ -alumina, (e) methanol-treated palmitic-acid-adsorbed γ -alumina (100 °C), and (f) γ -alumina regenerated with methanol solution (100 °C, 3 wt%).

Table 1. Palmitic acid methyl ester yields according to experimental conditions with 3 wt% sulfuric acid

No.	Temperature (°C)	Regeneration time (min)	Methanol-solution-to- γ -alumina weight ratio	Palmitic acid methyl ester yield (%)
1	60	30	10 : 1	87.95
2	80	30	10 : 1	90.41
3	100	30	10 : 1	97.06
4	100	30	2 : 1	9.18
5	100	30	5 : 1	89.87
6	100	30	25 : 1	97.75
7	100	5	5 : 1	85.10
8	100	15	5 : 1	87.08
9	100	45	5 : 1	99.9

**Fig. 10. Proposed acid-catalyzed regeneration mechanism of fatty-acid-adsorbed γ -alumina using methanol.**

catalyzed methanol regeneration, regardless of the regeneration time.

5. GC/MS Analysis of the Reaction Products

GC/MS analysis was used to analyze the reaction products of acid-catalyzed methanol regeneration and to obtain information about acid-catalyzed methanol regeneration mechanism. Palmitic acid methyl ester was the only detected reaction product, and Table 1 shows the yield of palmitic acid methyl ester formed during the acid-catalyzed methanol regeneration under various experimental conditions. These results demonstrate that adsorbed palmitic acid was transesterified to palmitic acid methyl ester by the reaction with methanol and sulfuric acid. The yield of palmitic acid methyl ester increased with increasing operating temperature, as shown in Fig. 3. At 100 °C, almost all of the adsorbed palmitic acid was converted to palmitic acid methyl ester when the methanol-solution-to- γ -alumina weight ratio was higher than 5 : 1 at a regeneration time of 30 min or more. Even when the regeneration time was less than 30 min, high yields of palmitic acid methyl ester were obtained, which is consistent with the TGA/DTG curves of regenerated γ -alumina shown in Fig. 6.

6. Proposed Mechanism of Acid-catalyzed Methanol Regeneration

It has been reported that fatty acids chemisorbed onto γ -alumina are desorbed through transesterification with supercritical methanol [15]. This is an energy-intensive process because of its

high operating temperature and the high methanol-to- γ -alumina weight ratio. Thus, a homogeneous acid catalyst was introduced to regenerate the palmitic-acid-adsorbed γ -alumina at a lower temperature than supercritical conditions, as shown in Fig. 10. The adsorbed fatty acids were converted to fatty acid methyl esters, which is a valuable fuel, by the transesterification mechanism. The detailed mechanism of acid-catalyzed transesterification is well known in the field of biodiesel production [17].

However, the methylation of the surface functional groups (Al-O-Al groups to form Al-OCH_3 and Al-OH), which occurs in supercritical methanol regeneration, was not observed in acid-catalyzed methanol regeneration, as shown by the TGA/DTG curves and FT-IR analysis. Possibly, the regeneration temperature was not sufficiently high to break the Al-O-Al covalent bonds because of their high bond dissociation energy.

7. Comparison of Methods for the Regeneration of Fatty-acid-adsorbed γ -Alumina

In our previous work, the regeneration of fatty-acid-adsorbed γ -alumina using supercritical methanol, which has several advantages to thermal regeneration, was introduced. In this work, a new energy-efficient γ -alumina regeneration method using methanol aided by a homogeneous acid catalyst has been developed. A comparison of three regeneration methods is presented in Table 2. Although the process of acid-catalyzed methanol regeneration is not

Table 2. Comparison of methods for the regeneration of fatty-acid-adsorbed γ -alumina

	Reactive desorption method		Thermal desorption method
	Acid-catalyzed methanol regeneration	Supercritical methanol regeneration	Thermal regeneration (or oxidation)
Temperature (°C)	100	300	550
Process	Complex	Complex	Simple
Adsorbed fatty acid	FAME (Biodiesel)	FAME (Biodiesel)	Decomposition
Catalyst	O	X	X
Surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Identical	Identical	Identical
Crystal structure	Identical	Identical	Identical

as simple as thermal regeneration, some merits of the acid-catalyzed methanol regeneration process were observed compared to the other methods. First, the acid-catalyzed methanol regeneration was carried out at the lowest operating temperature of the three regeneration methods, which means that this process consumes less energy than the other methods. However, the homogeneous acid catalyst was indispensable in acid-catalyzed methanol regeneration because of the low operating temperature. The second major difference is the by-product synthesized during the regeneration process. When adsorbed fatty acids are decomposed to volatile compounds, they can be released as air pollution during thermal regeneration. In contrast, during acid-catalyzed methanol regeneration, the adsorbed fatty acids are converted to fatty acid methyl esters, which are valuable fuels, through transesterification.

The crystal structure of the regenerated γ -alumina was unchanged in all three regeneration processes. However, the conversion of γ -alumina to aluminum sulfate occurred on some parts of the surface during acid-catalyzed methanol regeneration. Previously, the surface area of raw γ -alumina was found to be $205 \text{ m}^2 \text{ g}^{-1}$, and similar results were obtained after regeneration (thermal regeneration: $193 \text{ m}^2 \text{ g}^{-1}$, supercritical methanol regeneration: $200 \text{ m}^2 \text{ g}^{-1}$) [15]. An almost identical result was obtained in this study (acid-catalyzed methanol regeneration: $202 \text{ m}^2 \text{ g}^{-1}$).

CONCLUSIONS

A new regeneration method for fatty-acid-adsorbed γ -alumina using methanol and sulfuric acid was developed. Palmitic acid was selected as a model fatty acid, and the fatty acid adsorbed on γ -alumina was converted to palmitic acid methyl ester through transesterification. A batch-type reactor was used to investigate the optimum conditions, which were found to be 100°C , 3 wt% sulfuric acid, a methanol-solution-to- γ -alumina weight ratio of 5 : 1, and a regeneration time of 30 min. The acid-catalyzed methanol regeneration process is a promising method for the regeneration of fatty-acid-adsorbed γ -alumina owing to its advantages over existing methods.

ABBREVIATIONS

BET : Brunauer-Emmett-Teller

FAME : fatty acid methyl ester
 FFA : free fatty acids
 TG : triglycerides
 TGA : thermal gravimetric analysis
 XRD : X-ray diffraction
 FT-IR : Fourier transform infrared spectroscopy

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