Araştırma Makalesi - Research Article

Investigation of Lauric Acid Conversion with the STA Incorporated Heterogeneous Catalysts in the Liquid Phase Reaction

Veli ŞİMŞEK[1*], Kırali MÜRTEZAOĞLU[2]

*A*bstract- **In this study, firstly the synthesis of acidic catalysts was carried out by loading the active compound silicotungstic acid(STA) with dry (W/Si:10-50%) and wet (W/Si:10%) impregnation methods into MCM-41 support material. These synthesized catalysts were used in the production of mono-di and tri laurin. The amount of active substance in the synthesized catalysts was determined by the ratios of tungsten in STA and silicon in MCM-41 structure. Moreover, W/Si: 10% by weight of STA was applied to the support material after the calcination process was loaded by dry impregnation method. Brønsted acid (BA) and Lewis acid (LA) regions of synthesized catalysts were determined by DRIFT analysis. The catalytic activities of the catalysts were determined by a glycerol-lauric acid esterification reaction in a batch reactor. The effect of calcination and active compound ratio with reaction temperature on the lauric acid conversion and mono-di and tri laurin selectivity was investigated. Furthermore, the esterification reaction of glycerol with lauric acid was carried out under the same conditions in the presence of a commercial catalyst Amberlyst-21. The experimental results of the synthesized catalysts and Amberlyst-21catalyst were compared. The synthesized catalysts after comparison were observed that have high catalytic activity. Lauric acid conversion and monolaurin selectivity have been obtained with W/Si: 10% catalyst (dry impregnation method) 3/3/1 molar ratio at383K after 6 hours 95% and 88%, respectively. XRD analysis was conducted on calcined-uncalcined MCM-41support material. Moreover, the structural properties of synthesized catalysts after the esterification reaction were determined by SEM-MAPPING analysis methods.**

Key Words- **STA, Mono-Di And Tri Laurin, Lauric Acid, MCM-41, Dry-Wet Impregnation**

I. INTRODUCTION

Biodiesel is known as an important fuel alternative due to the use of renewable resources in its production. As biodiesel production has become widespread in recent years, researches have focused on the evaluation of glycerol as a byproduct during production. Glycerol is a byproduct occurs as 10% of biodiesel produced. In order to make biodiesel production economical and sustainable, it has become inevitable to evaluate the glycerol obtained [1]. When the studies about the evaluation of glycerol are examined, it is seen that glycerol has been used as a raw material in the etherification and esterification reactions in recent years [2]. Esters are formed by the change of the OR group in place of the OH group of carboxylic acids [3]. Homogeneous or heterogeneous acidic catalysts are used in industrial scale ester production. The acid catalysts used in the reactions catalyze the reaction by protonating to the carboxylic acid [4]. Homogeneous catalysts are generally used in esterification reactions [5]. Mineral acids such as H₂SO4, NaOH, HCl, and HI are conventional homogeneous catalysts [5-8]. The interest in heterogeneous catalysts has recently increased due to the rapid dissolution of homogeneous catalysts in the reaction medium, corrosion, environmental pollution and the need for a separation process [5, 8, 9]. DVB (divinylbenzene), amberlyst groups [8, 10], acidic zeolites and heteropoly acid catalysts are frequently used as solid acid(heterogeneous)catalyst [10].

¹*Sorumlu yazar iletişim: veli.simsek@bilecik.edu.tr, (https://orcid.org/0000-0002-3518-1572)
Department of Chemical Engineering, Bilecik Şeyh Edebali Univ., Bilecik, Turkey
²İletişim: kirali@gazi.edu.tr, (https://orcid.org/0000-0002-0810-2816)
Department of Chemical Engineering, Gazi Univ., Ankara /Turkey

Glycerol, a wide constituent of all animal and vegetable fats, is trivalent alcohol, in which oils are esterified with fatty acids, mostly in the form of glycerides. It is also produced in biodiesel and today plays an important role in meeting the industrial need. In addition to the different applications for technical purposes, especially in the processing of food materials and in the production of drugs, fat-derived glycerol is preferred [11]. Furthermore, glycerol is a very hygroscopic (moisture-absorbing) material, it prevents drying in the environment where it is used, especially in the cosmetic industry has become widespread usage. The most important feature sought in glycerol, which must be of very high purity, is that it contains absolutely no water [11]. And, glycerol esters have a common different of applications such as solvents, emulsifying, etc. The monoglyceride obtained as the desired product has applications as oiling agents in the food industry, as lubricants for plastics, pharmaceutical, and cosmetics industries and as emulsifiers in food [12, 13]. Monoglyceride selectivity has been obtained higher than 75% by esterification of glycerol with lauric acid and oleic acids [14].

There are several studies of glycerol esterification using different catalysts. Glycerol conversion and triacetylglycerol selectivity reached 97% and 13% with Amberlyst-15 at 383 K after 30 min. [15]. Another study, on the other hand, found a glycerol conversion of 97.1% with the highest triacetylglycerol selectivity (43.2%) over acidic Amberlyst-15, after 6 hours of at 383 K and using 9:1 acetic acid to glycerol molar ratio [16].

Lauric acid (dodecanoic acid) is a solid powdered fatty acid, which is saturated with 12 carbon atoms chain, is white in color, weakly laurel oil or soap smells. Lauric acid is a component of triglyceride, and about half of the lauric acid in the industry is derived from coconut oil and laurel oil [17].

In this study, it was aimed to evaluate the high acidic silicotungstic acid (STA)based catalysts synthesized by dry and wet impregnation method in the esterification reaction of the biodiesel by-product glycerol with lauric acid. The impregnation synthesis method is the fast, cheap and controlled method to prepare catalysts [18]. STA is an HPAs. Solid catalysts such as HPAs [19], metal oxides [20], zeolites [21] and ion-exchange resins [22], and have been used in liquid phase esterification reactions. Furthermore, HPAs have high Brønsted acid sites, which allow their use in etherification and esterification reactions [23]. HPAs are known for their high activity for esterification, etherification, etc. reactions. Although they have several disadvantages such as low surface area and high solubility in polar solvents such as alcohol, they are preferred in esterification reactions due to their chemical properties and their high catalytic activity [17, 24]. The STA needs support to increase its thermal stability in liquid phase reactions. The MCM-41, is selected as a support material in this study, since it has a large surface area, thermal stability, and very narrow pore size distribution and pore diameter can be adjusted between 15 and 100 Å. MCM-41 mesoporous, nano-structured catalysts were first synthesized by Mobil research group in 1992 [14]. The pore shapes of MCM-41 are two-dimensional hexagonal [17, 25, 26]. Therefore, mesoporous support materials can be utilized as a catalyst carrier [27] in various applications such as drug delivery systems[28]. However, pure MCM-41 mesoporous molecular sieves have disadvantages such as low hydrothermal stability, low catalytic activity and poor surface acidity in oil processing. For these reasons, researches have focus on MCM-41 modification in last two decades [16, 29].

Many catalysts with different properties are widely used to obtain industrial products. Catalysts are used to increase the efficiency of the reactants as well as to reduce the time required to complete the reaction and to ensure that processes are more economical and applicable. Studies with the catalysts in the literature are generally directed to the synthesis of catalysts which exhibit high catalytic activity, and also physically and thermally stable and reusable. Esterification reactions with equilibrium limitation are slow. Homogeneous or heterogeneous catalysts are used to improve esterification reactions and increase productivity. Recently, heterogeneous catalysts are preferred due to their easier removal from the reaction media and their corrosion free nature [9, 30].

In this study, the catalytic activities of the synthesized catalysts were investigated by esterification reaction of lauric acid with glycerol (glycerol/ lauric acid/ ethanol) in a batch reactor. The effect of temperature on the conversion of lauric acid to mono-di and trilaurin selectivity in esterification reactions was investigated. One of the important aims of this study is to investigate the effect of calcined and un-calcined MCM-41 support material porosity and surface area on lauric acid conversion and mono-di- tri laurine selectivity. Another purpose of this paper was to determine whether the catalysts synthesized by using in the same reaction conditions, since the commercially available Amberlyst-21 catalyst has an industrial field of usage. In addition, the effect of esterification reaction on synthesized catalysts was investigated by SEM and MAPPING analysis methods.

II. MATERIAL AND METHOD

A. Synthesisof MCM-41Support Material

In this study, MCM-41 support material was first synthesized by hydrothermal method. 13.2 g of cetyltrimethyammonium bromide (CTMABR; $C_{19}H_{42}BrN$-Merck) are dissolved in 87 ml of deionized water and the temperature of the resulting solution is kept constant at 30°C and stirred continuously. This process is continued until a clear solution is obtained. The silica source (Sodium silicate- Merck, Na_2SiO_3; containing 27% SiO_2) is then added drop wise to the solution. After adjusting the pH of the solution to around 11(H_2SO_4-Merck), it is stirred for an hour. The mixture is then placed in steel autoclave with a Teflon container and left in the oven at a temperature of 120 °C for 96 hours. After 96 hours, filtration is performed to separate the sample from the gel. The solid sample obtained after the filtration is washed with distilled water by vacuum filtration until the pH value is stabilized at about 7. Then the sample is dried at 30 °C for 18 hours. In the final step of the synthesis, the calcination is carried out in a quartz reactor in a dry air environment, at 550 °C during 6 hours [30]. The STA was loaded with dry and wet impregnation methods before and after calcination into support material.

B. Synthesis of STA/MCM-41Catalysts

The STA/MCM-41 catalysts were synthesized by modification of the procedures of Varışlı (2007). The schematic presentation of the synthesis of STA/MCM-41 catalysts is shown in Figure 1.The active compound ratio in the STA/MCM-41 catalysts was the mass ratio of the tungsten in the STA structure to the silicon in the sodium silicate structure. Within the scope of the study, the active compound ratios for the STA/MCM-41 catalyst were determined as W/Si: 10, 50%. Synthesis steps are given as follows:

Synthesis Steps:

1. Calcined or non-calcined MCM-41 support material is mixed with 12 ml deionized water at 200rpm and at 30°C.

2. Wet impregnation: STA was dissolved in distilled water before it was added to the support solution. Then, the solution of STA was added drop wise to the support material solution.

3. Dry impregnation: STA was added directly to the support solution.

4. The solidified sample is allowed to dry for 24 hours at 70°C, 21 hours at 96°C and then at 120°C for 2 hours (to remove water in the structure of synthesis catalysts).

5. Calcination of the sample is carried out at 350°C (heat rate, 1°C/a minute) for 6 hours using a quartz glass tube with a membrane filter [32].
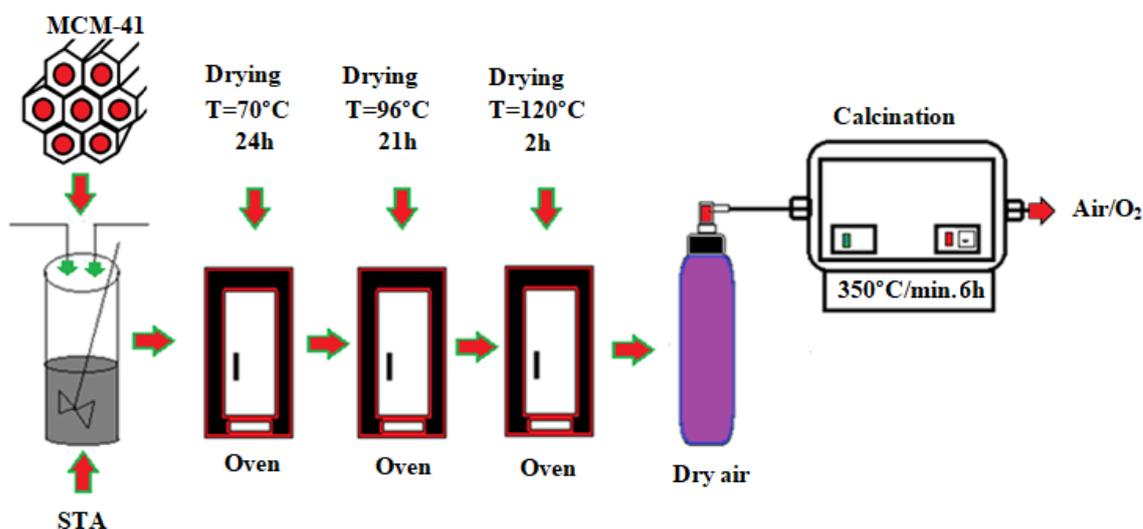

Figure1. The synthesis procedure of catalyst STA/MCM-41(W/Si: 10, 50% un-calcined dry impregnation, W/Si: 10% calcined dry impregnation, W/Si:10% un-calcined wet impregnation)

C. Characterization Studies

Surface structures characterization of the support material and catalysts, and elemental analysis of the were carried out using the Zeiss Supra V40 SEM instrument after platinum coating, by "SEM and MAPPING" analysis methods. In addition, BA acid and LA sites of the catalysts were investigated by using DRIFT analysis method after catalyst loading XRD samples of calcined and un-calcined of MCM-41 support materials were obtained by using Panalytical Empryran HT-XRD instrument. The analysis conditions of XRD were CuK$_\alpha$ radiation (λ=1.540Å) with 40 kV (current), 30V(tension), 0.066 step size and scanning angle (2Θ) from 0° to 50°.

D. Catalytic Activity Measurement

The catalytic activities of the synthesized catalysts and the commercial catalyst Amberlyst-21 were investigated in the esterification reaction with glycerol and lauric acid reactants. The reaction experiments were carried out in a batch reactor system operating at autogenic pressure. The reaction time was determined to be 6 hours for glyceride production. The experimental conditions of the reactions are given in Table1.

Table 1. Experimental conditions used in the production of glycerides.

Catalyst	Amount of catalyst(g)	Temperature (K)	Feed molar ratio	Run
Amberlyst-21	0.4	383	3/3/1	1
%10*	0.4	383	3/3/1	1
%10**	0.4	383	3/3/1	1
%50*	0.4	383	3/3/1	1
%10***	0.4	383	3/3/1	1
%10*	0.4	413	3/3/1	1

Un-calcined dry impregnation*, Calcined dry impregnation**, Un-calcined wet impregnation***

Analysis of the product and reactant mixture taken at certain time intervals during the reaction experiments were injected into the Shimadzu GC-2010 Gas Chromatograph and the conversion and selectivity values were determined (the operating conditions of the GC device are given in Table 2.). The esterification reaction with lauric acid by glycerol (Eq.1-3) is affected by 3 parallel reactions.

$$Glycerol + Lauric\ acid \rightarrow Monolaurin + H_2O \tag{1}$$

$$Lauric\ acid + Monolaurin \rightarrow Dilaurin + H_2O \tag{2}$$

$$Lauric\ acid + Dilaurin \rightarrow Trilaurin + H_2O \tag{3}$$

The conversion factor was calculated for the conversion of lauric acid and mono, di, and trilaurin selectivity and the calibration factors are based on this factor. The obtained factors were used to calculate lauric acid conversion and mono, di and trilaurin selectivity. The following equations were used for the conversion and product selectivity calculations. (Eq.4-7) [17].

$$Conversion\ \% = [(C_M + 2C_D + 3C_T)/(C_M + 2C_D + 3C_T + C_A)]x100 \tag{4}$$

$$Monolaurin\ selectivity\ \% = \left[\frac{(C_M)}{(C_M + 2C_D + 3C_T)}\right]x100 \tag{5}$$

$$Dilaurin\ selectivity\ \% = \left[\frac{(2C_D)}{(C_M + 2C_D + 3C_T)}\right]x100 \tag{6}$$

$$Trilaurin\ selectivity\ \% = \left[\frac{(3C_T)}{(C_M + 2C_D + 3C_T)}\right]x100 \tag{7}$$

Here, C_M, C_D, C_T, and C_A correspond to mono-laurin, di-laurin, tri-laurin, and lauric acid concentrations, respectively [17]. Concentrations were calculated separately with "response factors (RF)" for each product and reactant. In the calculation of the response factor (Eq.8) was used [17]:

$$RF = \left(\left(\frac{A_X}{C_{IS}}\right)X\left(\frac{A_{IS}}{C_X}\right)\right). \tag{8}$$

Where:

A_x= Peak area of the component

C_x= concentration of the component

A_{is}= Peak area of internal standard

C_{is}= Concentration of internal standard

The reactants and product mixture were tested using Shimadzu GC-2010 gas chromatograph. Hydrogen (99.9%) and dry air (99.9%) were fed for the temperature adjustment (temperature program: 353K-603K) of flame ionization detector (FID; 653K) and the column (Restek Rtx-1, 30mx0.32mmx0.1 μm capillary column). Nitrogen (99.9%) was used as the carrier gas at constant pressure (58, 0 KPa). The liquid reactant was injected manually (sample volume; 0.2 μl) at a split ratio of 100% and column flow rate of 1. 5 mL/ min.

III. RESULTS AND DISCUSSION

XRD analyses were performed on the synthesized support material before and after calcination. The low-angle and high-angle XRD samples of MCM-41(calcined- un-calcined) are given in Figure 2. The main Bragg peaks of MCM-41 obtained at (100), (110), (200) and (210) reflections. According to the results, it was observed that the support materials had a regular hexagonal structure before and after calcination (Figure 2 and Figure 5(a,b) [32]. However, the low angle XRD analyses showed that shifts and intensity increase of some main Bragg peaks of MCM-41 were observed after calcination (Figure 2 b, c).
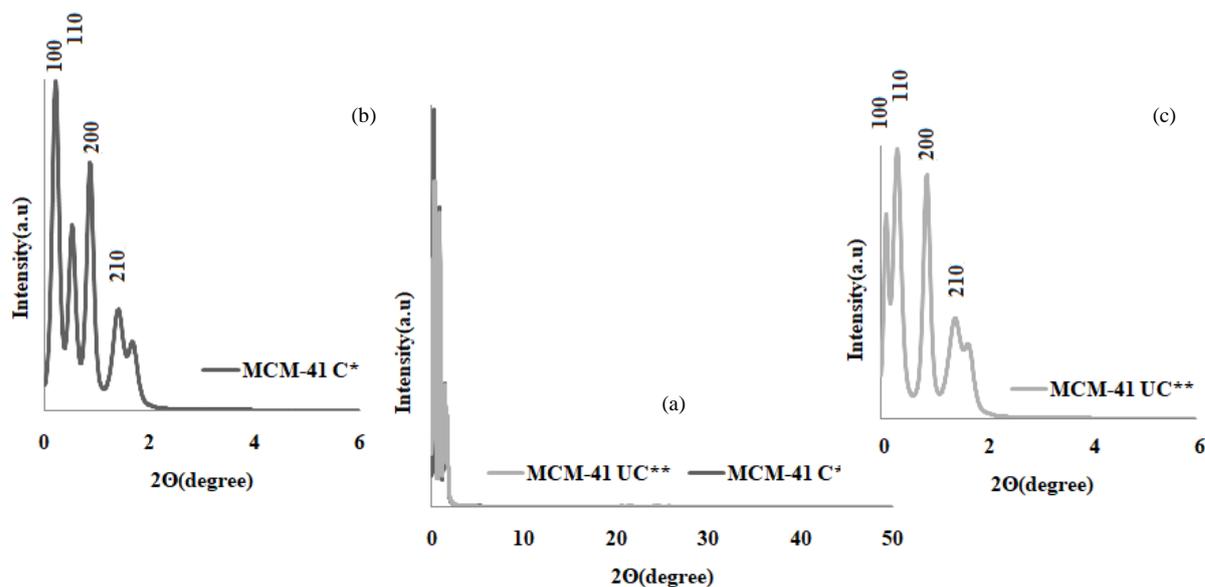

Figure2. Low angle(b, c) and high angle(a)XRD samples of calcined and un-calcined of MCM-41 support material

In order to determine the acidic properties of the catalysts, the DRIFT analyses were performed before esterification reactions. DRIFT analyzes of the samples covered with pyridine were carried out by FT-IR (Perkin Elmer instrument in the range of 1000-2000 cm^{-1}) after an hour. The DRIFT analysis method was used to determine the BA and LA sites of the catalyst. When the DRIFT analysis results were examined, increases in acidic parts were observed due to the loading rates of the synthesized catalysts. Three distinct peaks were observed at 1485, 1540 and 1612 cm^{-1}. The peaks at wavelengths 1612 and 1478cm^{-1} correspond to the BA and LA sites in the catalyst structure (Figure 3). The peak obtained at a wavelength of 1540 cm^{-1} shows the adsorbed pyridine in the catalyst structure [17, 24-26, 29, 33, 34].
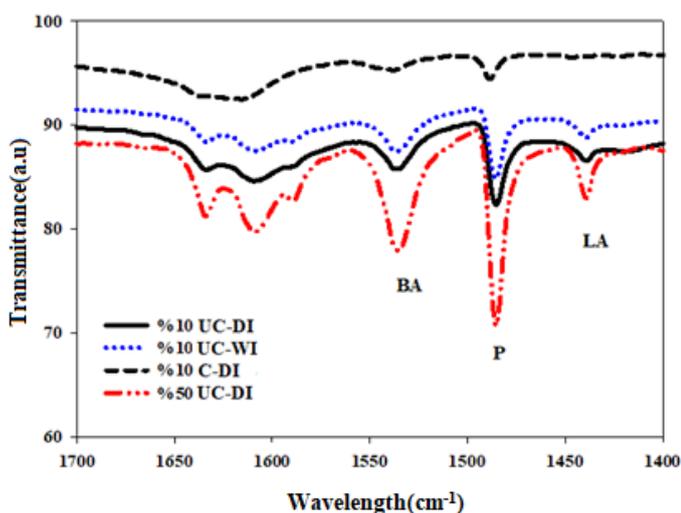
Figure3. Drift analyses of STA/MCM-41 catalysts (10% C-DI, UC-DI, Calcined and un-calcined dry impregnation, 10% UC-WI: Un-calcined wet impregnation, 50% UC-DI: un-calcined dry impregnation)

The results of SEM analyses of MCM-41 and STA /MCM-41 materials, which were synthesized before and after calcination were examined. Although the changes in the hexagonal structure of the MCM-41 support after the active compound loading were limited, an increase in these changes was observed after the esterification reaction of glycerol and lauric acid (Figure 4).
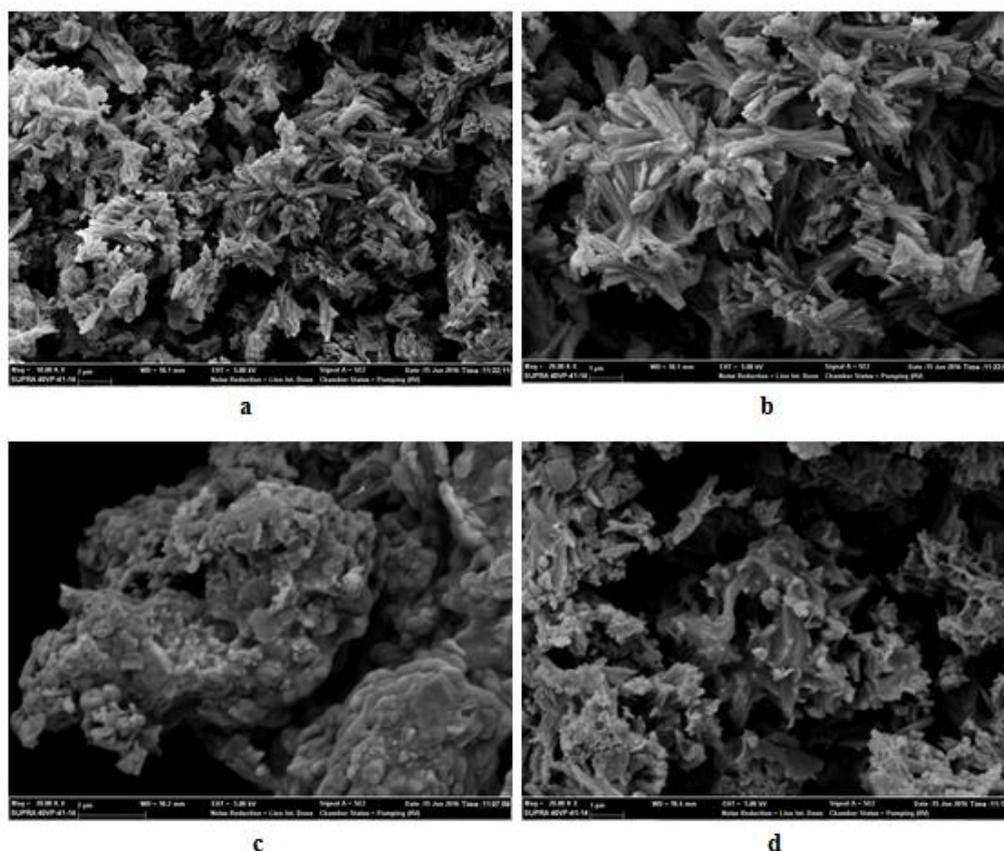
Figure4. SEM images of before un-calcined MCM-41 support material (a), (b); 10-20kx) and after glycerol/lauric acid esterification reaction of 10% STA/MCM-41 (UC-DI; un-calcined dry - impregnation) ;(c) 383K, 6 h, (d)413K, 6h).

MAPPING analyses were performed on samples obtained after glycerol/ lauric acid esterification reactions of STA/MCM-41 (W/Si: 10%, UC-DI). The reaction temperatures are 383, 413K and the reaction time is 6 hours. After the reaction, the samples were washed with 300 ml of distilled water, then dried at 6 hours at

reaction temperatures. According to the results of MAPPING analysis, it was observed that the silicon (Si) contained in support material (MCM-41) and tungsten (W) in the active compound (STA) maintained their homogeneous distribution (Figure 5).
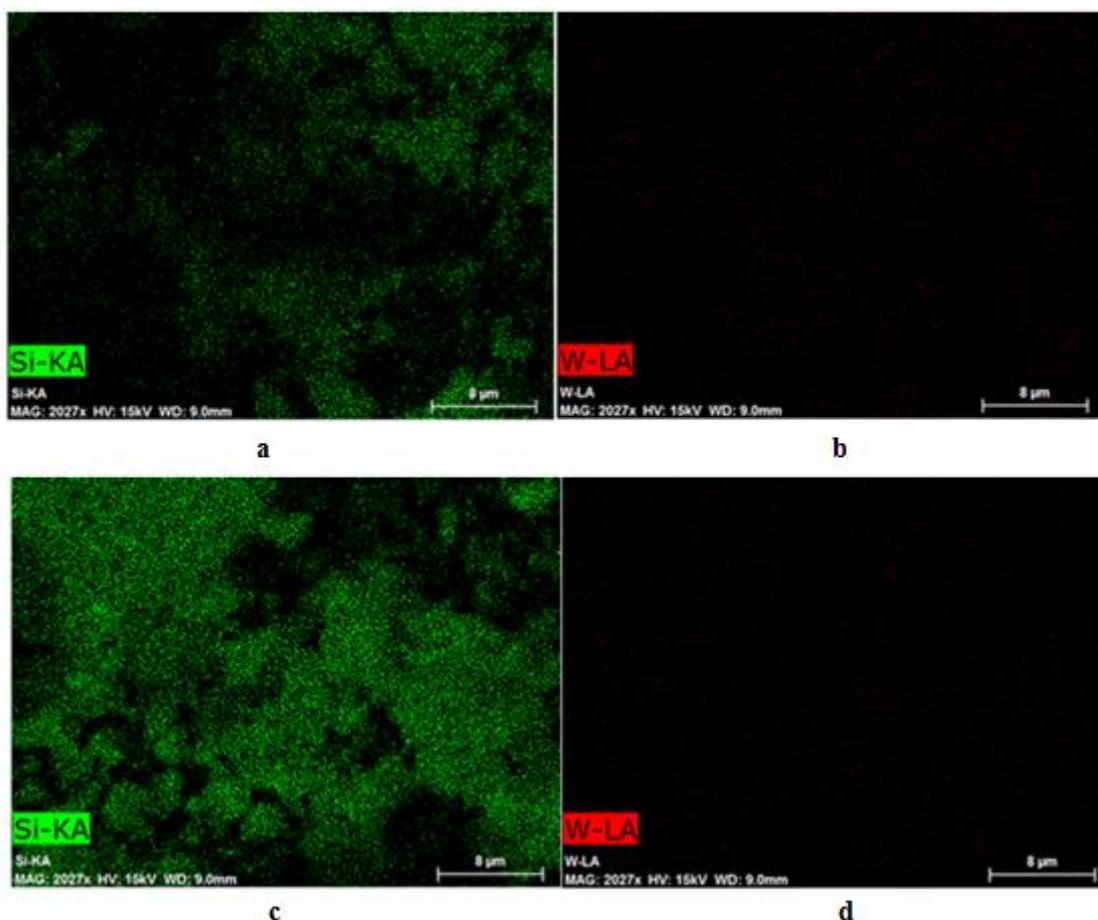

Figure5. MAPPING images of 10% STA/MCM-41(UC-DI) after glycerol/lauric acid esterification reaction. a, b) 383K, 6 h, c, d)413K, 6h).

The catalytic activities of the commercial catalyst Amberlyst-21 and synthesized catalysts (STA/MCM-41, W/Si: 10, 50% DI and 10% WI) were investigated in the glycerol/ lauric acid/ethanol esterification reaction. Moreover, the esterification reactions of glycerol/ lauric acid/ethanol were performed in a batch reactor at autogenic pressure. Firstly, glycerol-lauric acid esterification reaction experiments of synthesized catalysts and a commercial catalyst Amberlyst- 21 were carried out at 383K, in presence of 0.4g catalyst and molar ratios 3/3/1(glycerol/ lauric acid/ethanol). Conversion of the lauric acid and selectivity of mono-di and tri laurin after 6 hours were calculated as 93%, 88-4-8%, respectively (Figure 6-8).
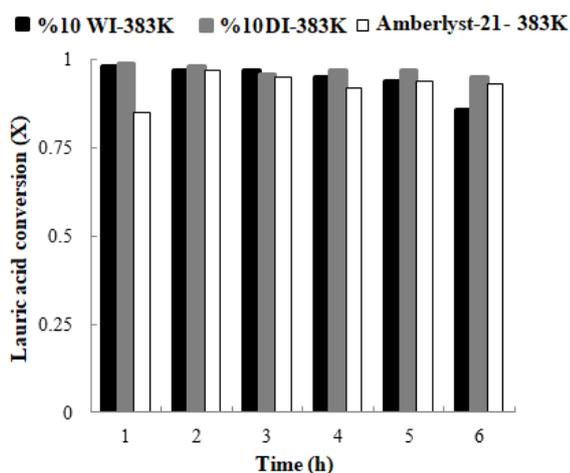
Figure6. Lauric acid conversion of synthesized catalysts and Amberlyst-21 (WI; Wet-impregnation, DI; Dry-impregnation, amount of catalyst: 0. 4 g, Molar feed ratio; 3/3/1).
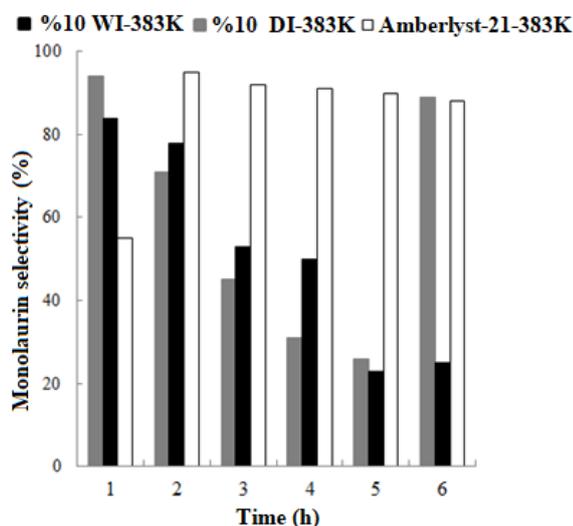

Figure7. Monolaurin of selectivity synthesized catalysts and Amberlyst-21(WI; Wet- impregnation, DI; Dry-impregnation, amount of catalyst: 0. 4 g, Molar feed ratio; 3/3/1).
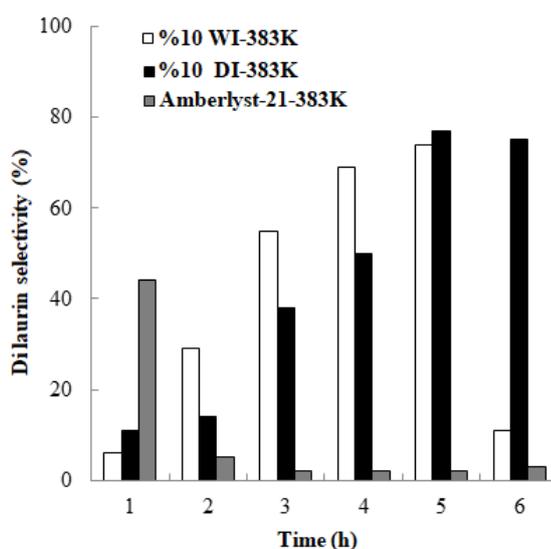

Figure8. Dilaurin selectivity of synthesized catalysts and Amberlyst-21(WI; Wet- impregnation, DI; Dry-impregnation, amount of catalyst: 0.4 g, Molar feed ratio; 3/3/1).

The effect of active compound loading ratio and calcination temperature on the conversion of lauric acid and mono-di and trilaurin selectivity were investigated. Lauric acid esterification reactions were carried out with synthesized catalysts before calcination (10%, 50% load, 383K, 0.4g catalyst, and 3/3/1 feed rate, during 6 hours). It was observed that the amount of active compound did not cause significant differences in conversion end of the 6 hours. However, significant changes in mono-di and tri laurin selectivity have been calculated (Figure 9, 10).

On the other hand, the effect of temperature on lauric acid conversion and mono-di and trilaurin selectivity was investigated in esterification reactions performed at 383 and 413K (0.4g catalyst and 3/3/1 feed rate, during 6 hours). Analysis results showed no significant change in-terms of conversion. But, significant decreases in the di-laurin selectivity have been determined. It was interesting to observe that mono-laurin selectivity increased (Figure 11, 12). However, the increase in the selectivity of tri-laurin was limited. The reason for this is the removal of water vapors formed in the reaction medium due to increasing temperature [12, 17, 30, 35]. Water in the reaction medium is an unavoidable, since it is a by-product in glycerol esterification. However, unless removed from the reaction medium, the increase in water amount as reaction proceeds results in leaching of active compounds into reaction medium and the decrease in triglyceride selectivity [36]. Its presence in the reaction medium helps to increase the rate of reverse reaction because of decreasing the selectivity of the end product. Competitive adsorption of water on active sites during reaction results in H_3O^+ formation leading to deactivation of the catalyst which is the main problem [37]. Activity decrease associated with water presence was also reported for palm oil hydrolysis [38].
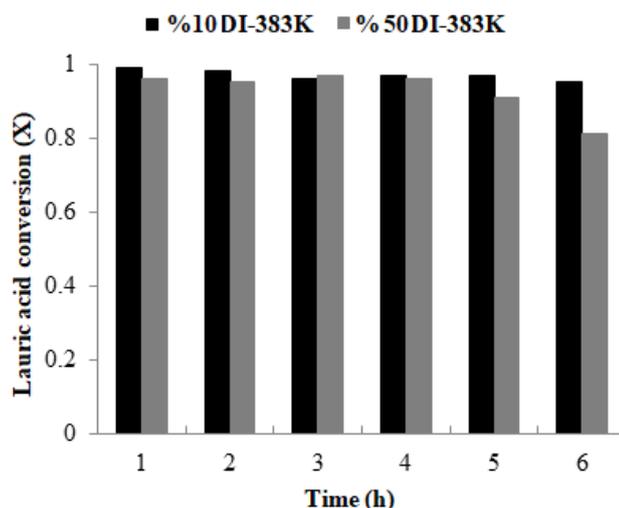

Figure9. Effect of the amount of active compound on the glycerol / lauric acid esterification reaction (DI; Dry -impregnation, amount of catalyst 0.4 g, molar feed ratio 3/3/1).
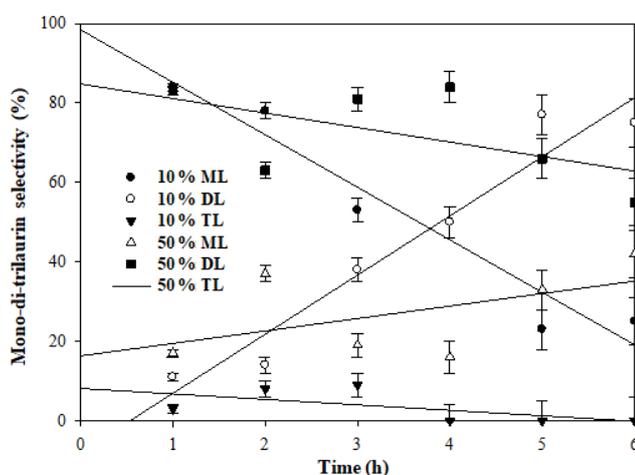

Figure10. Effect of the amount of active compound on mono-di and trilaurin selectivity (amount of catalyst: 0.4g, reaction temperature, 383K, dry impregnation before calcination).

As a result, the effect of calcination temperature on lauric acid conversion was limited. Before calcination under the same conditions, lauric acid conversions for calcined and un-calcined catalysts were 95% and 88%, respectively. There were no significant differences in lauric acid conversion in terms of active compound loading rates. Finally, there was no significant change in lauric acid conversion compared to the Amberlyst-21 catalyst, whereas the decrease in mono-laurin and an increase in di and tri laurin selectivity were observed.
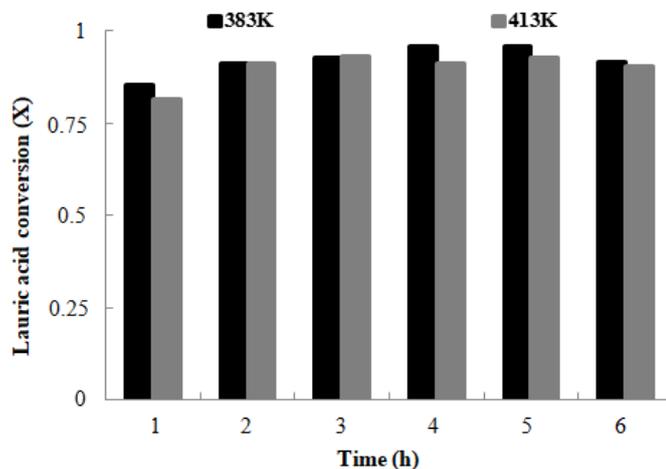

Figure11. Effect of the reaction temperature on mono-di and trilaurin selectivity (amount of catalyst: 0.4g, reaction temperature, 383-413K, dry impregnation before calcination).

Figure12. Effect of reaction temperature on mono-di and trilaurin selectivity (amount of catalyst: 0.4g, reaction temperature, 383-413K, dry impregnation before calcination).
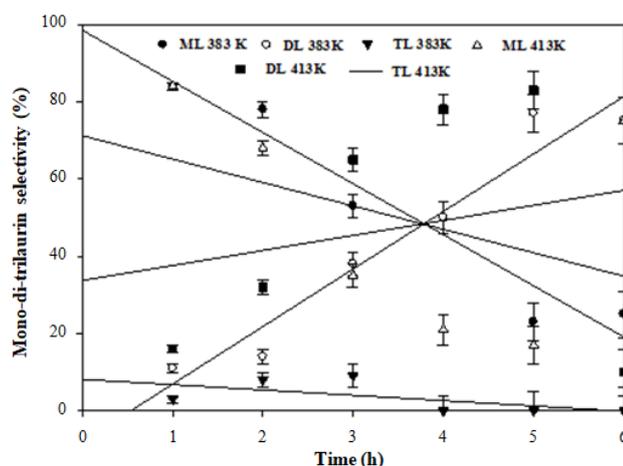
IV. CONCLUSIONS

In this study, the catalytic activities of the commercial catalyst (Amberlyst-21) and synthesized catalysts were investigated in the glycerol/lauric acid/ethanol esterification reaction. According to the experimental results obtained catalytic activity was high. When the glycerol/lauric acid esterification reaction was carried out at the temperature above the decomposition temperature of the Amberlyst-21 catalyst (413K), STA/MCM-41 (10%, DI before calcination) catalyst showed significant effect on the mono-di and trilaurin product selectivity.

As a result, the effect of synthesized catalysts by different (wet-dry impregnation) methods on lauric acid conversion and mono-di and tri laurin selectivity was determined to be limited. Similarly, the effect of the calcination temperature applied to the support material was limited to the lauric acid conversion and the mono-di and trilaurin selectivity (88% after calcination 95% before calcination). When the esterification reactions of synthesized catalysts and Amberlyst-21 catalyst were compared, no significant change was observed in lauric acid conversion, whereas mono-laurin selectivity decreased and di and tri laurin selectivity increased.

ACKNOWLEDGMENTS

LIST OF ABBREVIATION

BA	: Brønsted acid	LA	: Lewis acid
SEM	: Scanning electron microscope spectroscopy	FT-IR	: Fourier transform infrared
HT-XRD	: High-temperature X-ray diffraction	DRIFT	: Diffuse Reflectance
C_M	: Concentration of Mono-laurin	C_D	: Concentration of Di-laurin
C_T	: Concentration of Tri-laurin	C_A	: Lauric acid concentration
RF	: Response factor	W	: Tungsten
Si	: Silica	STA	: Silicotungtic acid
DI	: Dry impregnation	WI	: Wet impregnation
UC	: Un-calcined	C	: Calcined
°C	: Degree celcius		

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