Investigation of Catalytic Activity of a Sulfonated Aluminum-Based Metal-Organic Framework: Design of Oleic Acid Esterification With Response Surface Methodology

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Research Article

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Abstract

In this study, the synthesis of MIL-53(Al) (Material Institute Lavoisier, MIL) material, which is an aluminum-containing metal-organic framework (MOF) and generally produced using the solvothermal method was carried out by microwave method at different synthesis times (30-180 min) and temperatures (120-180 °C). In order to improve the catalytic activity of the MIL-53(Al), it was functionalized by applying sulfonation process and SO₃-MIL-53(Al) material was also provided. It has been observed that the changing in the synthesis time and temperature cause changes in the morphologies, surface areas and thermal resistance. The highest surface area value was obtained as 1256.3 m²/g at 180 °C-180 min synthesis condition. MIL-53(Al) and SO₃-MIL-53(Al) were investigated as catalysts for the esterification of the oleic acid with methanol by designing response surface methodology (RSM). The SO₃-MIL-53(Al) catalyst provided higher conversion of oleic acid to ester than MIL-53(Al) as 97.2% and 65.9%, respectively.

1. Introduction

Due to the increasing environmental concerns and strict regulations in the world, environmentally friendly and efficient catalytic technologies attract great attention. Liquid catalysts which are very important in the chemical and refinery industry are highly dangerous, corrosive, polluting and non-reusable in catalysis processes. For this reason, the development of highly porous solid catalysts with high activity and stability is highly desirable for both scientific and industrial aspects. Therefore, due to their high surface area, porosity and possibility to be modified and also effective usability in adsorption, separation and gas storage processes, in recent years, metal-organic frameworks (MOFs) are very popular especially in catalysis processes [1–3].

MOFs are two or three-dimensional porous structures formed by the combination of a metal (ion or cluster) and an organic binder [4]. As a subset of coordination networks, the main difference of MOFs is that they have potential voids [5]. Hundreds of different MOFs can be synthesized by replacing metal salts and organic linkers. This diversity of MOFs also enables them to be used in different application areas such as gas storage/capture, purification, separation, sensors, drug delivery, and catalysis [6–10]. There is a need for adding acidic or basic functional groups to the cage structure of MOFs, which will increase their efficiency especially in catalysis processes. Moreover, the effectiveness of MOFs in these application areas can also be increased by adding functional groups to MOFs.

MOFs are basically functionalized by two different methods: post-synthesis method (PSM) obtained by adding functional groups to MOFs structures after synthesis, and pre-functionalization method to obtain MOFs with ligands containing functional groups [11, 12]. The pre-functionalization method is more useful and simple than the PSM method, but the variety of the PSM method makes the PSM method more important. PSM is a highly effective technique for preparing topologically identical but functionally different lattice structures [13].

MOFs can be synthesized by many methods such as solvothermal, microwave, sonochemical, electrochemical, mechano-chemical [14, 15]. Generally, it is the most used is solvothermal method, because it is very useful and simple, but requires long synthesis time. The long synthesis time of the solvothermal method has increased the tendency towards alternative methods [16]. Therefore, the microwave method has become an important alternative in MOF synthesis due to its simplicity as well as the fact that the synthesis takes place in a very short time [17]. For many MOF structures, there is still no comprehensive study investigating the synthesis parameters such as temperature and time using the microwave method.

Thanks to their unique properties, the use of MOFs as catalysts has been widely studied in recent years. However, there are limited studies on the use of MOFs as catalysts in esterification which are also used in biodiesel production. Esterification process plays an important role in numerous applications such as polymers for industrial use, paints, polishes, medicines, fragrances, softeners, solvents, and synthetic rubber production [18]. Esterification reactions are carried out with the help of catalysts such as H_2SO_4 , HCl and H_3PO_4 homogeneous acid catalysts. Recently, these homogeneous acid catalysts have been replaced by heterogeneous catalysts due to the disadvantages of separation, corrosion, environmental and reusability. Thanks to the reusability properties of heterogeneous catalysts, serious environmental and economic benefits can be achieved. In recently, thanks to their unique properties in this field, MOFs have been used extensively as a solid catalyst [3, 18–21].

One of the MOFs, Al^{3+} , Fe^{3+} and Cr^{3+} based MILs (Materials of Institute Lavoisier) series can provide great advantage for esterification due to their high stability and available raw materials [22, 23]. In this sense, MIL-53(Al), an aluminum-containing MOF, stands out with its high thermal stability and low toxicity. In this study, the synthesis of MIL-53(Al), was synthesized using microwave method at different synthesis times and temperatures. In addition, the MIL-53(Al) material was modified with post-synthetic modification (PSM) to obtain the sulfonated structure of MIL-53(Al), $\text{SO}_3\text{-MIL-53(Al)}$. The catalytic activities of the synthesized MIL-53 (Al) and $\text{SO}_3\text{-MIL-53(Al)}$ were investigated as catalysts for the esterification of oleic acid with methanol by designing with response surface methodology (RSM). Performing the design of the experiment with RSM helps to determine the effect of process variables and the interactions between all variables and provides a better understanding of the process. The effect of process variables (MeOH/OA, catalyst amount, temperature and time) on the esterification reaction and determination of the optimum reaction conditions by RSM is also studied.

2. Material And Methods

2.1. Chemicals

For the synthesis of MIL-53(Al) structures; aluminum nitrate ($(\text{AlNO}_3)_3 \cdot 9\text{H}_2\text{O}$, Acros Organics, +99%), terephthalic acid (TPA, Acros Organics, +99%) and ultrapure water were used. Sulfuric acid (H_2SO_4 , Merck 98%), trifluoromethanesulfonic anhydride (Triflic anhydride, Tf_2O , Sigma Aldrich, +99) and nitromethane

(CH₃NO₂, Acros Organics, 96%) were used for the sulfonation process on MIL-53(Al). In the catalytic activity studies, an unsaturated fatty acid, 18-carbon oleic acid (OA, C₁₈H₃₄O₂, Acros Organics, 99%) and methanol were used for the esterification reactions.

2.2. Preparation of MIL materials

The synthesis of MIL-53(Al) was performed with the Microwave method by modifying the solvothermal method of Loiseau et al. (2004) [24]. 1 mmol Al(NO₃)₃·9H₂O and 1 mmol TPA were placed in 100 mL of teflon reactor with 30 mL of distilled water. The reactors were held in the microwave oven for the desired test temperature and time (120, 150, 180 °C and 30, 60, 120 and 180 min). At the end of the studies carried out at the specified time and temperatures, the reactors were cooled to room temperature. After reaching room temperature, it was washed with 80 °C DMF to remove unreacted Al(NO₃)₃ and TPA reagents and washed 3 times with methanol to remove DMF from the cage structure and centrifuged.

The sulfonation process on MIL-53(Al) (for 180 °C -180 min synthesis) was carried out by the post-synthesis modification method using nitromethane (CH₃NO₂) solvent in the presence of trifluoromethanesulfonic acid (triflic anhydride, Tf₂O) [25]. For the sulfonation process, MIL-53(Al)/H₂SO₄/ Tf₂O (1/1/1.5 molar ratio) were added into 10 mL of nitromethane and mixed for 60 min. Then, the mixture was filtered, the solid was washed 3 times with distilled water and once with acetone. The obtained sulfonated MIL-53(Al) material was kept in ethanol at 70 °C for 24 hours and then in vacuum at 100 °C for 12 hours.

2.3. Characterization of MILs

The Scanning Electron Microscopy (SEM) images and Energy Dispersive X-ray (EDX) analyzes of MIL materials were performed in the ZEISS Supra 55 brand scanning electron microscope. Samples were coated with platinum-palladium plating under vacuum for 15 minutes before analysis to obtain a better image. X-Ray Diffraction (XRD) analyses were performed with a Rigaku Smartlab brand powder XRD device at 2-theta angle between 3⁰-30⁰ with XRF mode open at 2°/min scanning speed. The FTIR spectra of the samples were recorded using with Perkin Elmer/MIR spectrophotometer and a Pike Technologies Gladi ATR accessory within the range of 450–4000 cm⁻¹, at a resolution of 1 cm⁻¹. Nitrogen adsorption isotherms were measured at -196 °C using a Micromeritics Tristar Orion II 3020 surface area and porosimetry analyzer. According to the resulting isotherms of the MIL-53(Al) samples, Brunauer-Emmet-Teller (BET) and Langmuir methods were used for the analysis of surface areas. Thermogravimetric analysis (TGA) were performed on a Mettler Toledo TGA/DSC 3+ thermogravimetric analyzer from room temperature to 600 °C at a ramp rate 10 °C/min.

2.4. Surface acidity

Surface acidities of synthesized MIL-53(Al) and SO₃-MIL-53(Al) materials was determined by potentiometric titration of n-butyl amine [26, 27]. This measurement provides information on the acid

regions of the catalyst relative to the E_i values of the initial electrode potential [26]. For measuring surface acidity, 200 mg of catalysts was shaken in 20 mL of acetonitrile (ACN) for 3 hours. The suspended material was then titrated with 0.02 N, 0.05 mL of n-butyl amine. Electrode potential change was measured with a digital pH meter in mV mode. The initial electrode potential indicates the acid strength of the catalyst.

2.5. Design of Esterification Experiments with RSM

Esterification reactions are affected by temperature change, reaction time, catalyst amount and alcohol concentration. These variables can either increase or decrease the conversion of fatty acids to esters. Therefore, it is important to determine the most favorable reaction conditions for the conversion of fatty acids to their esters and also to evaluate the influence of process variables to maximize yield and reduce costs in the ester production. The catalytic activity of the prepared catalysts was tested for the esterification of oleic acid with methanol. To optimize the esterification process, experiments were designed according to the response surface methodology (RSM) by using the Design Expert-12 statistical program. The most basic experimental design model is central composite design (CCD) which is used in the RSM. Central composite design consists of $2k$ (k is the number of independent parameters) factorial points consisting of two axial points on each axis and some central points at a distance α (α) from the center of the design. Different α , i.e., different CCD can be obtained by taking the distance of the axial point from the center of the design. In this design, depending on the factor of k , the number of experiments (N) was determined by the following formula:

$$N = 2^k + 2k + 6 \quad (1)$$

The experiments were carried out according to a central composite design with six center points for each catalyst resulting in 30 experiments. The level selection was determined according to the results obtained in pre-tests. The independent parameters of molar ratio (x_1), catalyst concentration (x_2), temperature (x_3) and time (x_4) were operated in the range of 20-100 mmol/mmol, 1-5 %, 70-150 °C, 30-180 min, respectively. The codes and levels of the independent variables are given in Table 1.

Esterification studies were also carried out by the microwave process. Before the esterification experiments, the MOF materials were stored in the oven at 105 °C for 12 hours. In each study, 10 mL of alcohol was kept constant and the molar ratio and catalyst concentration were determined. At the end of each study, the MOF was separated from the liquid phase with 0.2 micron filters and ester conversions were determined by Gas Chromatography-Flame Ionization Detector (GC-FID, Agilent 7890A, HP Innowax column 30m*250 μ m*0.25 μ m). The percent of conversion of oleic acid to ester were determined by using equation 2 from the areas of the obtained chromatograms.

$$\text{conversion to ester \%} = \frac{\text{Ester peak area}}{\text{Theoretical ester full conversion peak area}} \times 100 \quad (2)$$

2.6. Reusability

Reusability studies were carried out for each catalyst at the central points of the experimental program prepared with CCD (molar ratio: 60 mmol alcohol/mmol FA, catalyst amount: 3 %, temperature: 110 °C and time: 120 min). After each run, the catalysts were recovered by centrifugation and washed 3 times with methanol. The recovered catalysts were dried under vacuum at 70 °C and their reusability was investigated in 3 repetitions.

3. Results And Discussion

First of all, MIL-53(Al), one of the MOF structures, was synthesized at different temperatures and times with the microwave method instead of the common solvothermal method in order to examine the change in synthesis yield of the materials and their textural properties. Then, the sulfonation process was performed to optimum MIL-53(Al) structure and catalytic activities of both MIL-53(Al) structures were investigated for the esterification process.

3.1. Characterization of MIL-53(Al) Materials

Microwave method production parameters of the synthesized MIL-53(Al) catalyst at different temperatures and times are given in Table 2. Pressure and power values naturally increased with the increasing temperature applied in the production of 100 mL closed Teflon reactors. The general reaction of the MIL-53(Al) formation and the obtained MOF structure is shown in Fig 1. As can be seen in the formation reaction of the MIL-53(Al) structure, H^+ concentration and therefore the acidity of the reaction solution will increase with the increase of conversion rate to MIL-53(Al). The final pH values measured after synthesis and also the calculated synthesis yield values confirm this result (Table 2). When the synthesis time and temperature increased, the synthesis yield of MIL-53(Al) is increased, but the more increase at the time and temperature, MIL-53(Al) cannot be obtained. White crystals which is specific to MIL-53(Al) could not be obtained at temperatures above 180 °C. It was not suitable for the microwave method over 180 min.

3.1.1 SEM-EDX analysis

SEM images of the materials obtained in the synthesis of MIL-53(Al) at different temperatures and times are given in Fig. 2 (a-m). Synthesized MIL-53 (Al) appears as a trapezoidal crystal, similar to those previously reported in solvothermal method [28, 29]. In Fig. 2, while the lowest crystal sizes (300-500 nm) are observed in the synthesis at 180 °C for 30-180 minutes, it is seen that the crystal sizes are between 500-800 nm in the synthesis at 120 °C for 180 minutes. It has been reported in the literature that over-micron crystal sizes are obtained in the synthesis of MIL-53(Al) by the solvothermal method [30, 31]. SEM image of SO_3 -MIL-53(Al) material obtained by functionalization after synthesis is given in Figure 2m. There is no significant change in the morphology and particle size of the MIL-53 (Al) material after the sulfonation process.

The EDX results of the synthesized MIL-53(Al) materials are given according to atomic percentages in Table 3. Elemental composition and distribution analysis by EDX measurement shows the presence of Al, C and O elements in synthesized MIL-53 (Al). Considering MIL-53 (Al) with the molecular formula $\text{Al}(\text{OH})\text{-}[\text{O}_2\text{C-C}_6\text{H}_4\text{-CO}_2]$, the % atomic C/Al and C/O ratios are compared to the theoretical ratios (theoretical C/Al and C/O ratios of 8.0 and 1.6, respectively). It can be said to be closer for materials synthesized at temperatures of 180 °C. The presence of element S in the EDX results of $\text{SO}_3\text{-MIL-53 (Al)}$ confirms the sulfonation process. The C/S ratio shows that 54% of the aromatic terephthalate units are successfully sulfated, assuming that there is mono-sulfonation to the MIL-53(Al) structure.

3.1.2 XRD analysis

The XRD spectra of the MIL-53 (Al) structure and the sulfonated $\text{SO}_3\text{-MIL-53(Al)}$ structure are shown in Fig 3. In the XRD spectra of MIL-53(Al), the peaks at $2\Theta = 9.3, 12.5$ and 17.8 degrees are among the basic peaks of MIL-53(Al) [2, 32, 33]. Peak intensities confirm the high crystallinity. Also, the XRD spectrum of the sulfonated material shows that the MIL-53(Al) lattice integrity is preserved. Sulfonated MIL-53(Al) material appears to have characteristic peaks at $2\Theta = 9.3, 12.5$ and 17.8 degrees in the XRD spectrum [25, 34] reported in the literature.

3.1.3 N_2 Adsorption Isotherms

It is important to determine textural parameters such as surface areas, pore volumes, average pore size and pore size distributions in MOF characterization. The BET surface area, Langmuir surface area, total pore volume and average pore diameter of MIL-53(Al) and $\text{SO}_3\text{-MIL-53(Al)}$ materials calculated from N_2 adsorption isotherm data are given in Table 4. The highest BET and Langmuir surface areas of MIL-53(Al) were obtained at 180 °C -180 min synthesis as 1256.3 and 1404.3 m^2/g , respectively. The BET surface area for MIL-53(Al) ranges from 1000 to 1600 m^2/g in the literature [24, 35–37]. Theoretically, MIL-53(Al) has a surface area of 1632.8 m^2/g [33]. The pore diameters of MIL-53(Al) materials vary between 14-16 Å and their total pore volume between 41-57 cm^3/g [32, 36, 37]. This shows that the synthesized MIL-53(Al) materials has been produced in large pore form. It is seen that the increase in synthesis time and temperatures cause some increase in pore volumes and diameters. The specific surface area and pore volume of the $\text{SO}_3\text{-MIL-53(Al)}$ were lower than those of the non-functionalized MIL-53(Al), especially the 180 °C-180 min synthesis. The BET surface areas has decreased from 1404.3 to 136.2, the pore volume from 0.56 to 0.23 and the pore diameter from 16.21 to 14.50. Although the sulfonated MIL-53(Al) structure have not differ as morphologically from the MIL-53(Al) structure, the surface areas and pore volumes have changed significantly.

Fig. 4 shows the nitrogen adsorption isotherm of MIL-53(Al) (synthesis 180 °C-180 min) and $\text{SO}_3\text{-MIL-53(Al)}$ structures. In Fig. 4, it is seen that the nitrogen adsorption capacity has significantly reduced after sulfonation. The isotherms obtained by nitrogen adsorption of MIL-53(Al) crystals are similar to the Type I isotherm. The similarity of the isotherms to the Type I isotherm model confirms that the synthesized

crystals have a microporous structure. isotherms [36, 38]. As given in Fig. 4 show that the materials have a microporous.

3.1.4 Thermogravimetric analysis

The proportion of organic or inorganic impurities attached to the lattice structure can be determined by thermogravimetric analysis depending on the loss of weight [39]. Fig. 5 shows the TGA curves of the MIL-53(Al) and SO₃-MIL-53(Al) materials. As seen in the TGA curves of MIL-53(Al) materials performed at 120, 150 and 180 °C for 180 min, the weight loss of structures occurred in 3 steps with a similar trend. Weight loss in the first step in the temperature range 60-120 °C; 5.1% for 120 °C synthesis, 3.4% for 150 °C synthesis, 4.3% for 180 °C synthesis. This result is due to the transition of water or solvent molecules in the pore or on the surface of the lattice structure to the gas phase [40]. The second step weight loss was determined at temperatures between 120-540 °C, around 2.1% and 1.0% for synthesis at 150 °C and 180 °C, respectively, and a little more 5.4% for a temperature of 120 °C. This loss of weight is due to the removal of organic and inorganic impurities due to the cage structure. The lower values obtained in 120 °C production in BET surface area measurements confirm the TGA result of the lattice structure produced at 120 °C. It shows that the channels and pores in 120 °C production cannot be completely free of impurities. The weight loss in the third step was between 540-580 °C, similarly between 34-37% of the total weight for the three substances. This step is the stage where TPA begins to decompose and the cage structure begins to degrade. The TGA curve of sulfonated MIL-53(Al) material (Fig. 5) shows that the structure is thermally stable up to a temperature slightly above 300 °C. After this temperature, it is seen that the cage structure has completely deteriorated. The first step weight loss was 45.8% at a temperature of about 300 °C. Then, weight losses in 4 different steps up to 568.7 °C, respectively, 9.4%, 364.5 °C, 9.2%, 419.5 °C, 8.2%, 474.4 °C and 21.6%, 568.7 °C has been realized. The first step is thought to be due to the degradation of the TPA binder while the other steps are due to various impurities and Al compounds. Thermal resistance of MIL-53(Al) material has decreased significantly after sulfonation.

3.1.5 FTIR analysis

The FTIR spectra of the MIL-53 (Al) obtained at optimum condition (180 °C-180 min) and SO₃-MIL-53(Al) structures is shown in Fig 6. In the MIL-53(Al) spectrum, the coordination of TPA organic ligand and Al metal centers is observed with asymmetric -COO stress in the 1601 cm⁻¹ band and symmetric -COO stress in the 1415 cm⁻¹ band. The stress in the region of 3672 cm⁻¹ is due to the μ 2-OH stress of the AlO₆ octahedra structure [24, 41–43]. The FTIR spectrum of SO₃-MIL-53(Al) shows similarities to non-sulfated MIL-53(Al). In the SO₃-MIL-53(Al) spectrum, the asymmetric and symmetrical -COO stresses observed in the MIL-53 (Al) material are observed in the band 1601 and 1415 cm⁻¹, respectively. Unlike pure MIL-53 (Al) material, the O=S=O tensile vibration in sulfated material was detected in the band of 1006 cm⁻¹. Again, it can only be explained by the settlement of the peak sulfoxy groups in the benzene rings, which appear in the 929 cm⁻¹ band in the sulfated sample [25, 34].

3.1.6 Surface acidity

Based on the initial electrode potential value of the catalysts, the amount of acid sites and their relative acid strength can be estimated. N-butylamine is a strong base and can be attached to acid sites of different strengths and types, so it will titrate both the Lewis and Brønsted sites [27, 44]. Potentiometric titration curves of MIL-53(Al) materials obtained with n-butylamine are given in Fig 7. Acid strength of these sites can be classified as: $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites), $100 < E_i < 0$ mV (weak sites) and $E_i < 100$ mV (very weak sites) [26]. According to this classification, it can be said that MIL-53 (Al) and SO₃-MIL-53 (Al) materials have very strong acid sites. The initial electrode potential (E_i) of SO₃-MIL-53(Al) (313 mV) material is quite high compared to MIL-53(Al) (116 mV). In processes such as esterification, the effectiveness of catalysts depends more on the active acid sites they have. This indicates that SO₃-MIL-53(Al) will have higher catalytic efficiency than MIL-53(Al).

3.2 The use of MIL-53(Al) and SO₃-MIL-53(Al) as catalysts in the esterification studies

3.2.1 Effect of process parameters for the response surface methodology

Esterification is an important class of organic reactions used to produce esters from organic acids and alcohols. The catalytic efficiencies of the synthesized MIL-53(Al) and SO₃-MIL-53(Al) catalysts were investigated by using microwave in the esterification experiments of oleic acid with methanol. The esterification reaction of oleic acid (OA) to methyl oleate (MO) by methanol (MetOH) is shown in Equation 3.

The experimental program was created with the central composite design (CCD) and molar ratio (x_1), catalyst amount (x_2), temperature (x_3) and time (x_4) was defined as coded variables. The MO conversion % (y) was defined as the response of the process for esterification of oleic acid with MIL-53 and SO₃-MIL-53 catalysts. The obtained results from CCD were given Table 5. Statistical Model Fit Summary suggested that oleic acid esterification fits the quadratic model for MIL-53(Al) catalyst and the 2-factor interactions (2-FI) model for SO₃-MIL-53 (Al).

The obtained model fitted equations for esterification of oleic acid (OA) with MIL-53(al) and SO₃-MIL-53(Al) were shown in equations 4 and 5.

$$y_{MO\%} = 1.21x_1 + 3.04x_2 + 10.12x_3 + 3.06x_4 - 1.79x_3^2 + 47.91 \quad (4)$$

$$y_{MO\%} = 1.729x_1 + 2.262x_2 + 11.22x_3 + 3.870x_4 - 1.79x_3x_4 + 74.41 \quad (5)$$

where x_1 : molar ratio MetOH/OA (mmol/mmol), x_2 : catalyst amount (%), x_3 : temperature (°C), x_4 : reaction time (min). The methyl ester conversion % (y) was defined as the response of the process. When the effects of independent variables on the answers in two equations are examined, it is seen that the parameters x_1 , x_2 , x_3 , and x_4 have positive effects on the system. The coefficients in the equations show that the most effective variable is temperature. The qualities of the models were also evaluated with the

analysis of variance (ANOVA) and results were given in Table 6. Model F values are obtained as 150.33 and 82.45 for MIL-53(Al) and SO₃-MIL-53(Al), respectively, indicate that the models are significant. Generally, the magnitude 0.01% of F values comes likely from noises. The models p values less than 0.050 indicate that model terms are important. In this case, x_1 , x_2 , x_3 , x_4 and x_3^2 for MIL-53(Al), x_1 , x_2 , x_3 , x_4 and x_3x_4 for SO₃-MIL-53(Al) are important model terms. Also, in the esterification of oleic acid with MIL-53(Al) and SO₃-MIL-53(Al), the signal-to-noise ratio of 47.916 and 33.791 obtained is quite sufficient. It is desired that the signal-to-noise ratio showing the model sensitivity is greater than 4.

In Fig. 8 a, b, comparison of experimental results with predicted results is given for MIL-53(Al) and SO₃-MIL-53(Al) ester conversions. It is seen that the experimental results and the model results are in agreement. In addition, R (R²adj) values, which is the other indicator of model conformity for MIL-53(Al) and SO₃-MIL-53(Al) catalysts, were found to be 0.969(0.962) and 0.945(0.933), respectively.

3.2.2 Influence of individual parameters

Perturbation plots given in Fig. 8 c, d show the individual effects of independent variables on response. The response of one factor was plotted by keeping the other factors constant at the center point. In both graphs for MIL-53(Al) and SO₃-MIL-53(Al), the steeper temperature curve compared to the other curves shows that the response is more sensitive to temperature. For MetOH/OA molar ratio, it is seen in Fig. 8c that the increase in the MetOH/OA molar ratio does not cause a significant change in the response, especially for MIL-53(Al).

The interactive effect of temperature and reaction time of methyl oleate conversion at a constant molar ratio (60 mmol MetOH/mmol OA) and catalyst amount (3% for MIL-53(Al) and SO₃-MIL-53(Al)) is shown in contour and 3-D plots in Fig. 9(a-d). In Figures 9 a and b, it can be seen that the conversion efficiency of MIL-53(Al) increases with increasing reaction time and temperature. It can also be seen in Fig 9 c and d that the conversion of methyl oleate does not change significantly with increasing reaction time at a constant temperature of 150 °C. On the contrary, it is observed that the conversion to methyl oleate significantly increases with the increase in reaction time for 70 °C temperature. This shows that the efficiency of the reaction time decreases as the temperature increases in the esterification studies with the SO₃-MIL-53(Al) catalyst.

3.2.3. Optimization of esterification reaction conditions

Optimum conditions for the esterification of oleic acid with MIL-53(Al) and SO₃-MIL-53 catalysts were determined by Design Expert 12 software numerical optimization. In order to obtain maximum ester conversions (response), all independent parameters (x_1 , x_2 , x_3 and x_4) were set to in the test range and are shown in Table 7. In the test range, the maximum ester conversions with MIL-53 and SO₃-MIL-53 were determined from the model results 63.5% and 91.6%, respectively. It can be seen in Table 5 that the experimental results are quite consistent with the model results. This confirms that model results can predict experimental results. In Table 5, the model results obtained by adjusting the independent variables

as minimum and the ester conversion as maximum and the experimental results also confirm the model fit.

3.3 Comparison of catalytic effects of MIL-53(Al) and SO₃-MIL-53(Al) catalysts

According to the results obtained, SO₃-MIL-53(Al) material showed higher catalytic efficiency in the esterification of oleic acid with methanol than MIL-53(Al). This shows that in esterification reactions with MIL-53(Al) catalysts, surface acidity is effective rather than surface areas of catalysts. With MIL-53(Al) and SO₃-MIL-53(Al), the highest ester conversions were obtained as 65.9% and 97.2%, respectively, in studies conducted at temperatures of 150 °C. Table 8 presented examples of the use of some heterogeneous catalysts at different reaction conditions in the esterification of fatty acids. Catalyst amount, reaction temperature, alcohol/fatty acid ratio and reaction time are known as important parameters in esterification process. In the esterification process, the suitability of these parameters to the process should be evaluated in the selection of the appropriate catalyst. According to the heterogeneous solid catalysts used in the literature, it can be said that MIL-53(Al) catalysts are effective in ester conversions. Especially the conversions over 90% obtained with SO₃-MIL-53(Al) material are well above the average. Although the high conversion to methyl oleate with MIL-53(Al) catalysts at high temperatures, the use of low catalyst amount is an important advantage.

3.4. Reusability of catalysts

One of the most important desired properties of heterogeneous catalysts is their stability in the reaction medium; the catalyst must be recyclable and reusable. Therefore, the reusability of MIL-53(Al) materials was studied in a series of three replicates and the results of all three experiments are shown in Fig 10. Reductions in conversion efficiency were observed in performing the esterification process of MIL-53(Al) and SO₃-MIL-53(Al) catalysts at the end of three reuses. This reduction can be explained by the closure of active sites by impurities. In esterification of OA with methanol, at the end of the third rework, the percent of conversions decreased from 46.8% to 42.3% for MIL-53(Al) and from 77.2% to 61.4% for SO₃-MIL-53(Al), respectively. These results are nevertheless satisfactory given the important advantages of heterogeneous solid catalysts over homogeneous liquid catalysts.

Conclusions

The synthesis of MIL-53(Al) has been generally carried out by the solvothermal/hydrothermal methods at 220 °C for 72 hours. In this study, MIL-53(Al) synthesis was performed using a microwave method at lower temperatures and duration. It was determined by SEM-EDX, XRD, surface area, TGA and FTIR analysis that the optimum MIL-53(Al) structure can be obtained at the 180 °C-180 min synthesis conditions. Especially, TGA and surface area results showed that the structure reached its purest form in studies performed at 180 degrees. As a detail, it was determined in the synthesis studies performed with microwave in water that the crystal sizes (300-500 nm) were decreased compared to the solvothermal method.

The catalytic activity of the obtained MIL-53(Al) and SO₃-MIL-53(Al) structures was evaluated by using the response surface method in the esterification experiments of oleic acid with methanol. According to the results obtained in the same experimental program created with CCD, the higher ester conversions were realized with the SO₃-MIL-53(Al) compared to the MIL-53. This shows that in esterification reactions with MIL-53(Al) catalysts, surface acidity is more effective rather than surface areas of catalysts. For MIL-53(Al) and SO₃-MIL-53(Al) materials, it has been observed that the molar ratio MetOH/OA (x_1), catalyst amount (x_2), temperature (x_3), reaction time (x_4) coded parameters positively affect the esterification process according to the approximation functions obtained from RSM. It was determined that the most effective independent variable among the approximation function coefficients was temperature. The highest conversions were obtained as 65.9% and 97.2% for MIL-53(Al) and SO₃-MIL-53(Al), respectively, in studies performed at temperatures of 150 ° C.

It was also determined that the catalytic activity of MIL-53(Al) catalysts was slightly decreased in reusability studies. However, MIL catalysts have important advantages in terms of industrial use such as adjustability, synthesis with affordable molecules and composite formation. Considering these advantages, the results obtained with MIL-53(Al) catalysts in the esterification of oleic acid with methanol are quite satisfactory. As a result, this study investigating the synthesis, functionalization and characterization of MIL-53(Al) material, which is an Al-containing MOF, by using water at different temperatures and times with Microwave method has presented very important data to the literature.

Declarations

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Tables

Table 1. The levels and codes of independent parameters in the Central Composite Design (CCD).

Parameters, symbols	Coded levels				
	-2	-1	0	+1	+2
Molar ratio (alcohol/FA, mol/mol), x_1	20	40	60	80	100
Catalyst concentration (%), x_2	1	2	3	4	5
Temperature, (°C), x_3	70	90	110	130	150
Time (min), x_4	30	60	90	120	150

Table 2. MIL-53(Al) synthesis parameters and microwave method operating conditions (Initial solution pH 3~3.5).

Temp.time °C-min	power watt	Pressure, psi	Synthesis yield %	Final pH
120-30	100-110	10-12	50.8	1.9
120-60	100-110	10-12	62.5	1.7
120-120	100-110	10-12	70.1	1.5
120-180	100-110	10-12	75.3	1.3
150-30	340-380	60-65	54.3	1.4
150-60	340-380	60-65	65.6	1.3
150-120	340-380	60-65	75.5	1.2
150-180	340-380	60-65	78.2	1.1
180-30	450-500	150-160	55.6	1.3
180-60	450-500	150-160	67.5	1.2
180-120	450-500	150-160	78.3	1.1
180-180	450-500	150-160	80.2	1.0

Table 3. EDX results of MIL-53 (Al) at different temperatures - times and SO₃-MIL-53(Al).

Temperature-time °C-min	C (% at.)	O (% at.) (C/O)	Al (% at.) (C/Al)	Pd (% at.)	Pt (% at.)
120-30	56.19	33.14 (1.69)	7.75 (7.25)	1.23	1.69
120-60	57.04	33.60 (1.70)	7.56 (7.54)	0.63	1.25
120-120	54.99	36.33 (1.51)	6.81(8.07)	0.62	1.24
120-180	55.93	33.85 (1.65)	8.67 (6.45)	0.45	1.41
150-30	56.60	34.61 (1.63)	7.41 (7.64)	0.38	1.18
150-60	57.39	33.86 (1.69)	7.85 (7.31)	0.36	1.14
150-120	54.82	35.88 (1.52)	7.71 (7.11)	0.37	1.46
150-180	55.04	36.01 (1.53)	7.47 (7.36)	0.38	1.09
180-30	56.07	34.64 (1.61)	7.35 (7.63)	0.47	1.47
180-60	56.23	34.50 (1.62)	7.46 (7.53)	0.42	1.40
180-120	55.52	34.77 (1.61)	7.59 (7.31)	0.47	1.63
180-180	56.88	35.42 (1.61)	7.39 (7.69)	0.43	1.69
SO ₃ -MIL-53(Al)	51.36	35.11	6.90 (S=3.69 %)	1.39	1.55

Table 4. Surface areas and porosity results of MIL-53(Al) at different temperatures - times and SO₃-MIL-53(Al) materials.

Temperature-time °C-min	BET surface area (m ² /g)	Langmuir surface area (m ² /g)	Pore volume (cm ³ /g)	Pore dia. (Å)
120-30	812.3	925.1	0.45	14.77
120-60	1042.2	1179.7	0.48	14.57
120-120	1083.3	1192.8	0.51	14.44
120-180	1088.7	1179.3	0.52	14.98
150-30	1098.7	1130.9	0.55	15.01
150-60	1122.2	1150.1	0.54	15.75
150-120	1139.3	1178.9	0.57	16.78
150-180	1192.6	1310.7	0.55	15.10
180-30	1230.1	1291.4	0.53	15.12
180-60	1220.9	1280.1	0.53	15.18
180-120	1208.7	1292.6	0.56	16.13
180-180	1256.3	1404.3	0.55	16.21
SO ₃ -MIL-53(Al)	136.2	164.2	0.26	14.50

Table 5. CCD experiment program and results.

run	Coded levels				Response (y)	
	x ₁	x ₂	x ₃	x ₄	MIL-53(Al)	SO ₃ -MIL-53(Al)
	mmol/mmol	%	°C	min	MO%	MO%
1	60	3	110	120	47.5	77.1
2	80	4	130	90	57.1	83.3
3	40	4	130	150	59.1	86.5
4	40	4	90	90	35.8	57.1
5	60	3	110	120	48.1	76.8
6	20	3	110	120	45.5	72.1
7	60	3	110	120	47.8	74.2
8	100	3	110	120	50.5	78.9
9	80	4	90	90	38.2	61.5
10	60	3	150	120	65.9	97.2
11	80	2	130	90	50.8	81.2
12	80	2	90	150	40.2	77.1
13	60	5	110	120	56.5	83.5
14	60	3	110	120	50.1	75.3
15	40	4	130	90	53.1	85.7
16	80	2	130	150	55.5	85.6
17	60	3	110	180	54.5	81.1
18	80	2	90	90	31.5	56.6
19	40	2	90	90	27.9	53.5
20	40	2	130	90	48.1	79.8
21	60	3	110	120	47.9	75.6
22	60	3	70	120	16.9	50.5
23	60	3	110	120	48.1	77.1
24	80	4	90	150	41.4	68.3
25	60	3	110	60	41.7	65.8
26	40	2	130	150	53.8	84.5

27	40	2	90	150	38.2	61.5
28	60	1	110	120	40.5	66.4
29	40	4	90	150	40.8	67.3
30	80	4	130	150	61.3	90.2

Table 6. ANOVA results of the models obtained by CCD

Source	MIL-53(Al)				SO ₃ -MIL-53(Al)			
	Sum of squares	df	F-value	P value	Sum of squares	df	F-value	P value
Model	3029.04	5	150.33	< 0.0001	3582.75	5	82.45	< 0.0001
x1	35.53	1	8.82	0.0067	71.76	1	8.26	0.0084
x2	220.83	1	54.80	< 0.0001	122.85	1	14.14	0.0010
x3	2456.33	1	609.55	< 0.0001	2977.05	1	342.54	< 0.0001
x4	224.48	1	55.71	< 0.0001	359.60	1	41.38	< 0.0001
x3x4	-	-	-	-	51.48	1	5.92	0.0228
x3 ²	91.88	1	22.80	< 0.0001	-	-	-	-
Residual	96.71	24			208.58	24		
Lack of fit	92.36	19	5.58	0.0329	201.64	19	7.64	0.0166
Pure error	4.35	5			6.95	5		
Cor Total	3125.75	29			3791.33	29		

Table 7. The predicted and actual values of the parameters and responses obtained from RSM for esterification of oleic acid with MIL-53(Al) and SO₃-MIL-53(Al) catalysts.

Parameters	X1 (mmol/mmol)	X2 (%)	X3 (°C)	X4 (min)	MIL-53(Al) MO %	SO ₃ -MIL-53(Al) MO %
	Min.	Min.	Min.	Min.	Max.	Max.
Predicted	40	2	112	90	41.7	68.0
Actual	40	2	112	90	40.1	65.8
	Test range	Test range	Test range	Test range	Max.	Max.
Predicted	80	4	130	150	63.5	91.6
Actual (run 30)	80	4	130	150	61.3	90.2

Min.:Minimum, Max: Maximum

Table 8. Comparison of the esterification studies with some heterogeneous solid catalysts.

Catalyst	Molar ratio (Alcohol/FA)	Alcohol/FA	time (h)	Temp. (°C)	Catalyst amount %	Conversion %
H-ZSM5 (Si/Al 25) [45]	16	MetOH :OA	1.5	60	1	80
ZSM5 [45]	4.5	MetOH:OA	2	70	10	76
H-Y-80[46]	3	MetOH :OA	3	100	10	92
S-OMC [47]	10	MetOH:OA	8	100	20	96
Amberlyst-BD20 [48]	6	MetOH:OA	3	80	16	93
Amberlyst-15 [48]	6	MetOH:OA	3	80	16	96
H-MFI (Si/Al=25)[49]	16	MetOH:OA	3	60	27	80
H-MOR(Si/Al=10)[49]	16	MetOH:OA	3	60	19	82
H-Y(Si/Al=5)[50]	6	EtOH: OA	2	200	19	74
%6 WO ₃ /H-Y(Si/Al=5) [50]	6	EtOH: OA	2	200	19	80
SBA15-C ₃ H ₆ -SO ₃ H [51]	160	MetOH: PA	3	85	10	80
SBA15-Ph-SO ₃ H [51]	160	MetOH: PA	3	85	10	93
Cs _{2.3} PW ₁₂ O ₄₀ [52]	30	MetOH:PA	3	60	1.9	73
Cs _{2.3} PW ₁₂ O ₄₀ [52]	30	MetOH:PA	6	60	1.9	100
Sulfated [SO ₄ ²⁻ /TiO ₂] [53]	10	EtOH:OA	2	80	2	69
Sulfated [SO ₄ ²⁻ /TiO ₂] [53]	10	EtOH:OA	3	80	2	83
SO ₄ ²⁻ /ZrO ₂ -MoO ₃ -Nd ₂ O ₃ [54]	9	MetOH:OA	2	65	10	90
SO ₄ ²⁻ /ZrO ₂ -MoO ₃ -Nd ₂ O ₃ [54]	9	MetOH:OA	4	65	10	98
MIL-53(Al)(this work)	60	MetOH:OA	2	150	3	65.9
SO ₃ -MIL-53(Al) (this work)	60	MetOH: OA	2	150	3	97.2

FA: Fatty acid, OA: Oleic acid, PA: Palmitic acid, LA: Lauric acid, MetOH: Methanol, EtOH: Ethanol

Figures

Figure 1

The formation of MIL-53(Al) and SO₃-MIL-53(Al)

Figure 2

SEM images of the materials obtained in the synthesis of MIL-53(Al) at different temperatures and times a) 120 °C-30 min, b) 120 °C-60 min, c) 120 °C-120 min, d) 120 °C-180 min, e) 150 °C-30 min, f) 150 °C-60 min, g) 150 °C-120 min, h) 150 °C-180 min, i) 180 °C-30 min, j) 180 °C-60 min, k) 180 °C-120 min, l) 180 °C-180 min, m) SO₃-MIL-53(Al)

Figure 3

XRD Spectra of MIL-53 (Al) synthesis materials a) 180 °C-30 min, b) 180 °C-60 min, c) 180 °C-120 min, d) 180 °C-180 min, e) 150 °C-30 min, f) 150 °C-60 min, g) 150 °C-120 min, h) 150 °C-180 min, i) 120 °C-30 min, j) 120 °C-60 min, k) 120 °C-120 min, l) 120 °C-180 min, m) SO₃-MIL-53(Al)

Figure 4

N₂ adsorption isotherm of MIL-53(Al) and SO₃-MIL-53(Al)

Figure 5

TGA curves of MIL-53(Al) (180 min at different temperatures) and SO3-MIL-53(Al)

Figure 6

FTIR spectra of MIL-53(Al) and SO₃-MIL-53(Al)

Figure 7

Potentiometric titration curves of MIL-53(Al) and SO₃-MIL-53(Al)

Figure 8

Comparison of experiment and model results in the CCD (a) MIL-53(Al), (b) SO₃-MIL-53(Al) and the individual effect of independent parameters for the esterification of OA with catalysts (c) MIL-53(Al) and (d) SO₃-MIL-53(Al)

Figure 9

Contour and 3D surface plot for the effect of reaction time and temperature towards methyl oleate conversion for (a), (b) MIL-53(Al) (c),(d) SO3-MIL-53(Al) (Conditions: molar ratio/OA= 60 mmol/mmol, catalyst amounts 3% for MIL-53(Al) and SO3-MIL-53(Al))

Figure 10

Reusability of MIL-53(Al) and SO₃-MIL-53(Al) catalysts