



# Synthesized 2nd Generation Zeolite as an Acid-Catalyst for Esterification Reaction

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## Abstract

MCM-48 zeolites have unique properties from the surfaces and structure point of view as it's shown in the results ,and unique and very sensitive to be prepared, have been experimentally prepared and utilized as a second-generation/ acid - catalyst for esterification reactions of oleic acid as a model oil for a free fatty acid source with Ethanol. The characterization of the catalyst used in the reaction has been identified by various methods indicating the prepared MCM-48 is highly matching the profile of common commercial MCM-48 zeolite. The XRF results show domination of SiO<sub>2</sub> on the chemical structure with 99.1% and agreeable with the expected from MCM-48 for it's of silica-based, and the SEM results show the cubic crystallographic space group compatible with Ia3d space group giving the hexagonal surface structure. The AFM test gave an average particle diameter of 97.51 nm and an average catalyst roughness of 0.855 nm. Esterification reaction of oleic acid with ethanol on MCM-48 has been carried in a batch reactor with 5% the prepared MCM-48 zeolite catalyst loading gives 81% of conversion after one hour at 353K

*Keywords: Biodiesel, Renewable Energy, Esterification, MCM-48 2<sup>nd</sup> Generation Zeolite*

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## 1- Introduction

The renewable fuels are growing progressively with time due to the limitation of conventional fossil fuel resources, increasing crude oil prices as well as concerns over environmental pollution and global warming [1].

The energy security is a very complicated standalone science and practice but can be rather over simplified by the energy resources diversification.

The energy requirements tend to increase the dependency on the renewable resources of energy, to promote the environmental protection and reduce greenhouse gas emissions.

Therefore, the energy security adoption led to the utilization of natural resources to generated energy that is from non-fossil bases (renewable energy), such as wind, solar, tidal, geothermal, and biomass derivative fuels [2].

The biodiesel is a promising fuel that competing the regular fossil diesel commercially.

The biodiesel produced from biomass oils and fats. Depending on the value of the feedstock acid number, biodiesel might produce either through transesterification or esterification reaction. Both homogeneous and heterogeneous catalysts commonly used in biodiesel production [2].

Heterogeneous catalysis provides a better activation energy path, and eliminates catalyst spent problem, plus it can be easily utilized for low quality feedstock with less concerns of catalyst deactivation or poisoning if undertaking proper process operation and pre-treatment of the reactants provided to contain sufficient amount of free fatty acid [2].

In esterification reaction the free fatty acid provides the hydroxyl group while the ethyl alcohol is the source of proton without an intermediate process [3]. Heterogenous catalysis differs from homogenous catalysis to undergoes a carbonium ion mechanism [4].

Heterogeneous catalysts are important for the development of biodiesel and have huge effect on the production cost. Over the years different type of solid base catalyst has been investigated such as metal complexes [5], [6], Metal hydroxides [7], metal oxides such as calcium oxide [8], magnesium oxide [9], zirconium oxide [10] and supported catalysts [11]. Solid catalysts are favorable over other catalyst type because they can be reused, regenerated and easily separated from product mixture. Zeolites and microporous are types of solids catalyst that have being widely applied in catalysis, their smaller pore dimension limits their application for larger molecules. One of the zeolite types are The MCM family materials, they have an ordered mesopores [12].

These materials have a well-defined pore. Pore diameter can be varied in the range of approximately 20-100 Å.

The main materials in the M41s family are hexagonal (MCM-41) and cubic (MCM-48). Both MCM-41 and MCM-48 have the potential to be used as catalyst in the esterification process. However, when comparing between MCM-41 with MCM-48, the MCM-48 provides easier access to guest molecules due to its three-dimensional pore network. The Structure of MCM-48 is cubic and has the space group  $Ia3d$  [13].

Also, mesoporous materials have very high surface areas with regular pore size dimensions which make them a good support as active phases. The functionalization of these mesoporous materials by active acidic or basic moiety several contributions were made by various researches [11-14]. The shorter diffusion distances in MCM-48 arising from the pore structure may influence the distribution of the tethered group over the surface during the functionalization process [14].

The work focused of the synthesis and characterization of a challenging new generation of zeolite MCM-48. Study the performance of the prepared catalyst in esterification of oleic acid.

## 2- Experimental Work

### 2.1. Material

- 1- Liquid colloidal silica, Ludox HS40 (39.5% SiO<sub>2</sub>, 0.4% Na<sub>2</sub>O, and 60.1% H<sub>2</sub>O by mass) as silica source
- 2- Hexadecyltrimethylammonium bromide HTABr (Aldrich) as surfactant
- 3- Industrial Alcohol 90% EtOH .
- 4- 1.0 molarity of Caustic Soda solution NaOH.
- 5- Washing HCl solution of 10% concentration by volume .
- 6- Distilled water H<sub>2</sub>O.

### 2.2. MCM-48 Catalyst Preparation

Colloidal silica (Ludox HS40) preheated to 343 K in an Erlenmeyer conical flask, then, the 1 M of caustic soda solution added slowly to the heated colloidal silica accompanied by vigorous magnetic continuous stirring (300 rpm). Then, waiting likewise till the solution reached clarity after approximately an hour of continuous stirring accompanied by heating to stay in the temperature range of 343-353 K

HTABr (Aldrich) was added to be dissolved completely till the solution becomes one phase by magnetic stirring and heating at 70°C (343 K) with 100 ml of diluted ethanol (60 wt.%). after that, combining both the surfactant solution with the sodium silicate solution.

Placing the sol-gel in the autoclave with continuous stirring for 4 days and heated to 373 K.

The supernatant liquid in the reaction mixture is cooled to 340 K and separated by vacuum filtration, the creamy solids on filter paper is washed with hot distilled water then with HCl-EtOH, sent to dryer set on 100°C (373 K) after proper filtration and then calcinated on an electric oven on 823 K aerobically.

### 2.3. Esterification Experimental Setup

The esterification reaction of oleic acid in batch reactor was undertaken in a batch laboratory scale reactor as shown in Fig. 1. The assembly apparatus used for the experiment consists of 500 ml three neck flat bottom glass flask operating as a batch reactor for the experiment reaction and an electrical heater with various temperatures regulator that was calibrated and set specifically for the reaction mixture in hand, with magnetic stirrer arrangement to achieve a perfect contact among the reactants.

The flask (batch reactor) was set in a manner that one side neck of it is plugged with air-tight rubber stopper that holds the thermometer used to enable monitoring the reaction temperature with the planned range of temperatures (40 to 70 C). The other side neck is used for tacking samples of the oil and alcohol catalyst mixture. The water-cooled condenser was inserted throughout the main neck of the reactor for purposes of the recovery of escaping ethanol that vaporizes at the elevated temperature during the reaction.

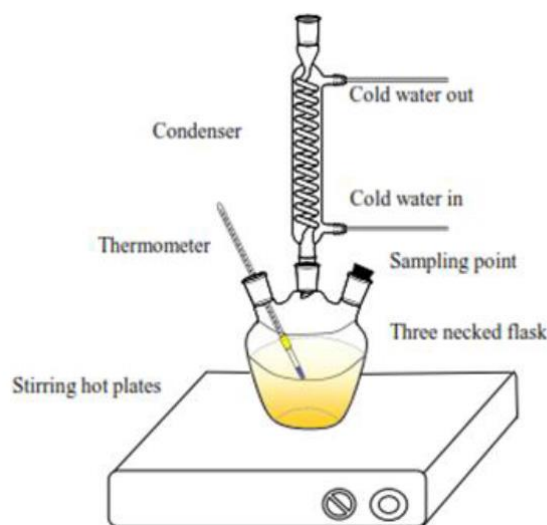


Fig. 1. Schematic diagram of the batch reactor for esterification

The required amount of catalyst (MCM-48) to be utilized in the experiment before each one was dried at 373 K for a period 2 h to eliminate any possible hydrate traces left on the surface of particles in inside the mesopores. At the beginning, the reactor was loaded with 50 ml (44.75 g) of oleic acid which was mixed with 6:1 ethanol to oil molar ratio. Then the reaction mixture was heated to 343 K and finally 5 wt. % of the prepared MCM-48 zeolite was added to the mixture to initiate esterification reaction.

The small samples of the mixture inside if the reactor which consist from the reactants, products and catalyst were piped out from the left neck of the reactor and tested after each time interval (15 minutes), approximately 5 ml from the reaction mixture was withdrawn and centrifuged for a period of 10 min to make sure of the separation of the phases specially the particles of catalyst, and then a certain amount from the top layer of product was taken and then added 2 drops of phenolphthalein as indicator for free fatty acid and titrate with 0.1 molarity of KOH in order to evaluate the acid value (AV) as it was given by [15].

$$AV = \frac{ml\ of\ KOH * N * 56}{Weight\ of\ Sample} \quad (1)$$

$$Conversion = \frac{AV_{to} - AV_t}{AV_{to}} \quad (2)$$

#### 2.4. Catalyst Test and Performance

The characterization of the prepared catalyst was carried through different method of analysis

##### a. X-Ray Diffraction (XRD)

Weight of sample is 3g in powder state, put in plastic cup 30 mm diameters. Test conducted in inert atmosphere. The XRD test was done in Geology Science Department – University of Baghdad.

##### X-Ray Diffraction Test Instrument

- 1- Using CuK $\alpha$  radiation Nickel filter ( $\lambda=1.54\text{\AA}$ ).
- 2- Data were collected within the  $2\theta$  range of  $1^\circ$  to  $5^\circ$  with a  $0.02^\circ$   $2\theta$ - step and 0.5s per step.
- 3- 30 Kv and 10mA X-ray diffraction was implemented to check the required patterns.

##### b. BET Surface Analyzer

Test Method according to ASTM D1993 for BET surface area and pore volume. The test reported by Petroleum Researchs and Development Center – Ministry of Oil.

##### c. X-Ray Fluorescence (XRF)

Weight of sample is 3g in powder state, put in plastic cup 30 mm diameters. Test conducted in inert atmosphere. The XRF test was done in Geology Science Department – University of Baghdad.

d. Scanning Electron Microscope (SEM): done in Chemistry Science Department – University of Baghdad.

e. Atomic Force Microscope (AFM): done in Physics Science Department – University of Al-Nahreen

### 3- Results and Discussion

#### 3.1. Characterization of Prepared MCM-48 Catalyst

Various techniques were undertaken in order to characterize the prepared second-generation acid zeolite, such as: X-ray Diffraction (XRD), X-ray Fluorescent Techniques (XRF), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM).

##### a. X-Ray Diffraction (XRD) Test result

The XRD uses the diffraction pattern to reveal the crystal structure of the prepared zeolite in order to undertake phase identification between the prepared zeolite and a reference diffraction of the same type (standard MCM-48).

Fig. 2 shows the diffraction pattern of the prepared zeolite alone to be compared with the standard.

The measurement was taken at angle range from 1 to 5. the measurements were taken under atmospheric conditions and the diffractometer was set with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

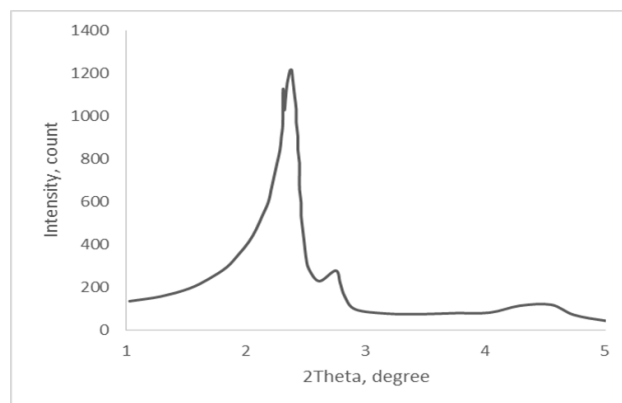


Fig. 2. XRD pattern for the prepared MCM-48 zeolite

The MCM-48 has only one peak in the x ray diffraction profile. This is true due to the fact that it compresses of one material only.

The diffraction pattern of the prepared MCM-48 is approximately matched with standard by comparing the peak position and the angle. The peak position of the standard MCM-48 is located at  $2\theta = 2.281^\circ$  with max intensity of 949 [16], since the highest peak of the was located at 2.316, which are very closed with the highest peak in the reported data of MCM-48 zeolite [16].

##### b. Surface Area and Pore Volume Calculation

The surface area and the pore volume of the prepared MCM-48 was measures using nitrogen adsorption and desorption method (BET). The measured value of the surface areas was  $669 \text{ m}^2/\text{g}$  and the pore volume was  $0.33 \text{ cm}^3/\text{g}$ .

## c. X-Ray Florescence (XRF) Analysis results

The chemical constituents of the prepared MCM-48 zeolites were analyzed using XRF technique, it was Table 1. The XRF analysis results of Chemical Constituents for the Prepared and MCM-48 Zeolites

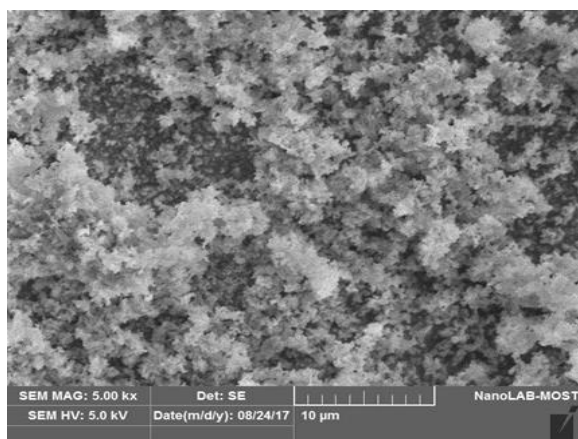
Oxides,	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	K <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>	other
wt. %	0.0038	99.1	0.0014	1.06	0.0034	0.0012	0.128	0.71	9.033

The silicon oxide (SiO<sub>2</sub>) was the dominant chemical structure with 99.1%. This is true because the MCM-48 is mainly silicon only and the XRF result is comparable with the XRD result in identify the prepared zeolite

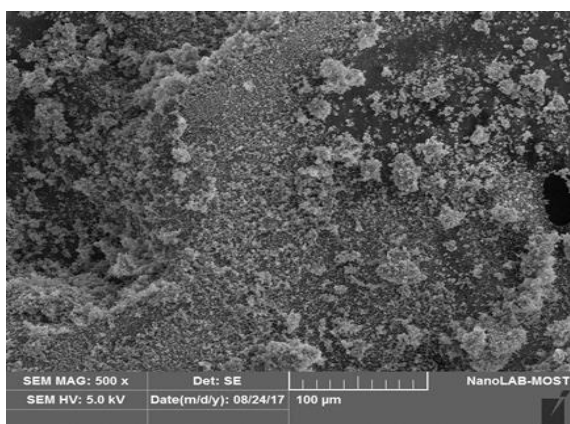
## d. Scanning Electron Microscope (SEM) results

The morphology of a sample from the prepared catalyst has been explored by using scanning electron microscopy (SEM) image. The SEM image was taken for 10 $\mu$ m, and 100 $\mu$ m respectively, as shown in images of Fig. 3.

The pattern is more obvious in the 10 $\mu$ m image indicates great structural order for cubic crystallographic space group compatible with Ia3d space group giving the hexagonal surface structure of an MCM-48 zeolite mesophase structure.



(a)



(b)

Fig. 3. SEM Results for the prepared acidic MCM-48 zeolite

important for chemical phase identification and to have a better view of the chemical structure. The chemical composition in weight percent is listed in the Table 1.

## e. Atomic Force Microscopy (AFM) Technique Results

The study of topography of the prepared catalyst is accomplished by using atomic force microscopy (AFM) device.

A high-resolution image for the surface of the catalyst has been carried. The AFM images can provide further information concerning the nature of the catalyst surface than the SEM. Average particle diameter was 97.51nm with which indicate that the prepared catalyst with in the Nano scale preparation [16].

Fig. 4 shows the histogram distribution of the particle size of the prepared MCM-48. The AFM show the accurate result of the average particle size which indicates the prepared zeolite is within the Nano range.

The particle distribution started from 40 with an average diameter of 97.51 nm ,10% of the distribution was for particles of 50 nm or less ,50% of the particles where 100 nm in diameter or less, and 90% of the sample were of 130 nm or less. The whole distribution occurs from 40 - 170 nm.

Topography image of the prepared zeolite is shown in Fig. 5, and Fig. 6 were both the 2D and 3D image were taken from the AFM analysis. The characterization of the catalyst was the average roughness as shown in figure 6 was 0.855 nm.

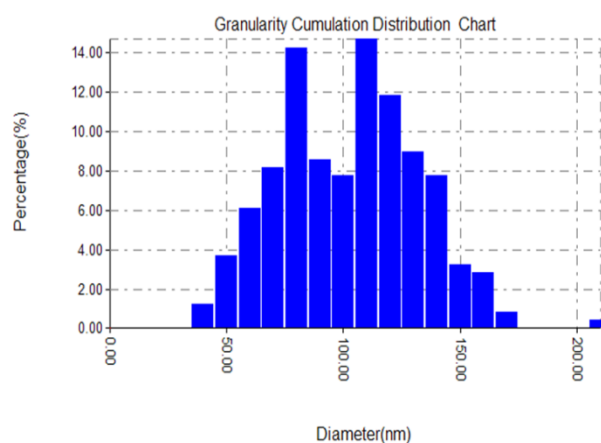


Fig. 4. Granularity Cumulative Distribution Chart for prepared MCM-48 zeolite



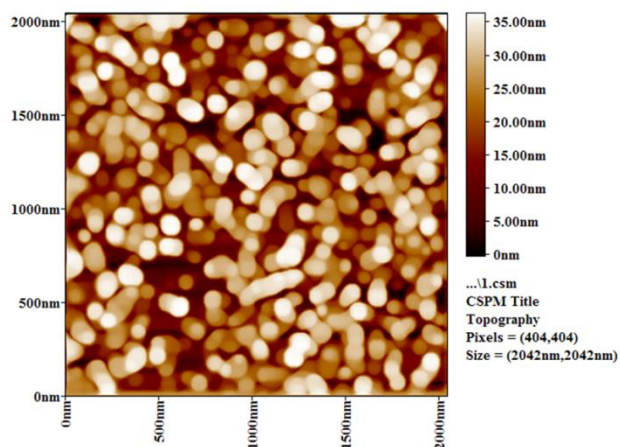


Fig. 5. 2D Topography images for the prepared MCM-48 zeolite

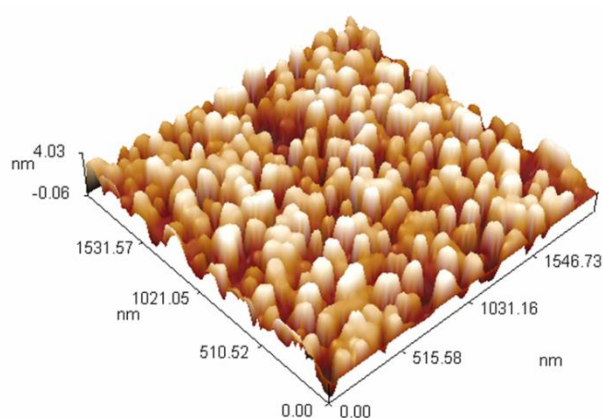


Fig. 6. 3D Topography images for the prepared MCM-48 zeolite

#### f. Effect of Esterification Temperature on Oleic Acid Conversion

Esterification reaction of the model oil (oleic acid) with ethanol occurs in the liquid phase, Effect of temperature for the esterification reaction has been studied with time as shown in Table 2. Temperature from 313-353 K has been studied and the experiment were operating for 60 min.

With MCM-48 catalyst the oleic acid conversion increases with increasing temperature have been calculated by equation 2. When temperature increases at each run, the oleic acid conversion will also increase for acid value range from 40 to 82.

When the temperature increases to 353 K, the oleic acid conversion increases double the increment value that has increased in the previous range after 60 min for all acid value.

At 353 K, 81% of oleic acid is converted after 60 min which it's the highest conversion reached in the experiment.

Table 2. Conversions of different temperatures of operation vs. time of reaction using acid number as an indicator of the amount of oleic acid reacted

Temperature [K]	Acid number of Oleic Acid*	Conversion%
313	119.42	40.58
323	106.53	47.00
333	82.41	59.00
343	38.19	81.00

\*Initial measured acid number value for Oleic Acid was 200

The study of temperature effect on the esterification reaction is important to determine the proper reaction condition. Also, according to Arrhenius's law the rate of reaction is temperature dependent. It's important to keep the reaction in the liquid phase and no vaporization occurs. So the selected temperature were 313, 323, 333 and 343 K and all the reaction material are liquid in this range indicates the oleic acid conversion with time at different temperatures as listed in the Table 2.

The conversion of oleic acid at the minimum temperature of the experiment 313 K is about 40%, while the conversion of oleic acid at 353 K is about 81%. One way to explain this temperature effect of that phenomena is, when temperature increases the viscosity of the reactants decreases, thusly, that will lead to improve the reactants penetration or the passage of the molecule through the pores of the catalyst due to bulk viscosity reduction and as a result the reaction would be taken place rapidly at the active site of the catalyst.

Another way to explain it, or in addition to the above, is by increasing the temperature providing more molecules with sufficient energy to cross the modified-by-catalyst energy barrier of the reaction and convert accordingly.

#### 4- Conclusion

The MCM-48 catalyst has been successfully prepared as second-generation acid-zeolite utilized for an esterification reaction catalyst. The characterizations of the catalyst used in the reaction has been identified by various methods indicating the prepared MCM-48 is highly matching the profile of common commercial MCM-48, the XRD gave the peak of standards MCM-48 located at  $2\theta = 2.281^\circ$  with max intensity of 949, since the highest peak of the was located at 2.316, which are very closed with the highest peak in the reported data of MCM-48 zeolite. The XRF results show the domination if SiO<sub>2</sub> on the chemical structure with 99.1% and that's agreeable with the expected from MCM-48 for its of silica based, And the SEM results shows the cubic crystallographic space group compatible with Ia3d space group giving the hexagonal surface structure. The AFM test gave an average particle diameter of 97.51 nm, 10% of 50 nm or less, and 50% 100nm or less, the 3D topography gave average catalyst roughness of 0.855 nm. The esterification reaction has been carried using the MCM-48.

The effect of acid value was investigated after 60 minutes of esterification at the apparatus that was utilized as a batch reactor, gave that at 353 K, the highest conversion of 81% has been gained.

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## تصنيع جيل ثاني من الزيولايت كعامل حامضي مساعد لتحفيز تفاعل الاسترة

علي حسين فتال و عمار صالح عباس

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### الخلاصة

تتميز مركبات الزيولايت MCM-48 بخصائص فريدة من حيث تركيب السطوح و البنية الجزيئية كما اظهرت النتائج ، اذ تم تحضيرها بشكل فريد و استخدامها كجيل ثاني من العوامل المساعدة لتحفيز تفاعل الاسترة لحامض الأوليك مع الإيثانول. تم تحديد خصائص المحفز المستخدم في التفاعل بواسطة طرق متنوعة، أشار فحص حيود الاشعة السينية إلى أن MCM-48 المحضر يتطابق بشكل كبير مع الزيولايت التجاري من نوع MCM-48 و أظهرت فحوص تظهر نتائج XRF هيمنة لمادة SiO<sub>2</sub> على التركيبة الكيميائية و بنسبة 99.1%. كما و بينت نتائج SEM تركيب بلوري مكعب متوافق مع مجموعة Ia3d و التي تعطي سطح سداسية بناء. أعطى اختبار AFM متوسط قطر الجسيم 97.51 نانومتر و متوسط خشونة سطح العامل المساعد 0.855 نانومتر. تم عمل تفاعل أسترة حمض الأوليك مع الإيثانول بأستخدام 5% من العامل المساعد المحضر في مفاعل دفعي و وصل تحول حامض الأوليك الى 81% بعد ساعة واحدة عند 353 كلفن

الكلمات الدالة: الوقود احبوي, طاقة متجددة, الاسترة