Catalytic Performance of Nanocrystalline Zeolite ZSM-5/MCM-41 composite for Production of Biodiesel

Asir Alnaama,Dr.Najwa Saber Majeed

Abstract— Nanocrystalline ZSM-5 and micro-mesoporous ZSM-5/MCM-41 composite zeolite were synthesized by hydrothermal treatment-conventional method. Micro-mesoporous ZSM-5/MCM-41 were synthesized using alkaline leaching (treatment) method and two step crystallization. Loading of synthesized composite zeolite with transition metals copper and cobalt was conducted by wet impregnation method. All zeolites products were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), Fourier transform infrared (FTIR), N_2 adsorption-desorption isotherm (BET), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).Nano level of average particle diameter was obtained of 50 nm. The catalytic performance of the catalysts were investigated in production of biodiesel by semi-batch esterification of alcohol (ethanol) with oleic acid, the conversion of 85% was obtained.

Index Terms— Alkaline Leaching, Biodiesel, Catalytic performance, Esterification, Nanocrystalline, ZSM-5, ZSM-5/MCM-41.

1 Introduction

Zeolite is a crystalline aluminosilicate with three dimensional sized pores of molecular opening **[1].** It is well known that zeolites play a vital role in catalysis world, as it is good support, besides it also have active sites, leading to play as bifunctional material. Catalyst and catalysis is a very important technology in solving the problems of energy and environmental issues to sustain our human society. Synthesis of catalyst in nano-level size improve its characteristics. It will give high specific surface area, better loading and distribution of active material and lead to better efficiency of the catalyst **[2].**Getting catalyst in nano-level size, must first prepare a support in nano-level size. Nanocrystalline zeolites are the target of many researchers during past decade **[1,2]**.

Synthesis of zeolite is conducted by thermal treatment and carried out in sealed autoclave (reactor), where an aqueous solution of alumina and silicone sources with structure directing agent (SDA) and other element is reacted at elevated temperature and at autogeneous pressure. There are static mode and stirring mode for the heated reaction mixture **[1]**. Stirring is very important for heat transfer and reaction rate and it is crucial for synthesis of some zeolite structure **[3]**. The drawback of zeolites is the diffusional limitation caused by small apertures (microporosity) in zeolite structure. Solving this diffusional limitation leads many researchers to develop a new methodologies, by either decreasing the particle size to nano-level in order not only to shorten the diffusion path length but also to increase the fraction of external surface area to total surface area of the zeolite and to have better accessibility for the reactant to reach the active sites in the catalyst, or introducing mesopores (2-50 nm) in the structure of zeolites to get good accessibility to the active sites inside the pores, leading to better mass transfer and higher reaction rate **[4]**.

One of the most interesting method for getting mesoporosity in microporous zeolite like ZSM-5 is alkaline treatment **[4]**, based on partial dessilication of ZSM-5 by aqueous solution of sodium hydroxide which will give more pores in the structure. MCM-41(Mobile composition of matter no.41) considered as mesopores molecular sieves and has unidimensional, presumed tube straight channel, with hexagonal unit cell and consist of a regular arrangement of cylindrical multiporous composite was successfully investigated by many researchers to get benefit from acidity and thermal stability of ZSM-5 and at the same time the mesoporosity of MCM-41 zeolite, **Song et al.,[5]** investigated the synthesis of MCM-41 composite from ZSM-5 zeolite by using alkaline leaching method by NaOH 1M solution then addition of 10% of cetyl trimethyl ammonium bromide (CTAB) as template (surfactant), the reaction carried on sealed autoclave, after pH adjustment. **Huiyong et al [6]** synthesized ZSM-5/MCM-41 micro-mesoporous composite zeolite by a two step crystallization using microwave radiation energy. **Nam et al.,[7]** studied the synthesis of multiporous (MC-ZSM-5/MCM-41) by two step, the first step to prepare the ZSM-5 seeds, the second step, is to add CTAB to ZSM-5 seeds then the gel was transferred into autoclave at 150 ^{o}C and 10-15 h.**Tang et al [8]** investigated the synthesis of ZSM-5/MCM-41 composite used alkaline leaching method with different concentration of alkaline solution from 0.5 to 3.5 M and two step crystallization using CTAB as template, they got BET surface of 435 m^2/g and pore volume of 0.4 cm^3/g. with acidity of 0.785 mmole/g NH_3 comparing with 0.915 mmole/g NH_3.

Biodiesel is considered as a green fuel, eco-friendly, and as an alternative for diesel fuel and derived from renewable sources **[9]**. It is chemically consists of alkyl esters of high fatty acids like fatty acid methyl ester and fatty acid ethyl ester. Biodiesel is produced widely by homogeneous transesterification of animal fats, vegetable oils in presence of either strong acid or basic solution, like sulphuric acid or sodium hydroxide. Its production by homogeneous transesterification has many

• *Dr.Asir Alnaama is lecturer in dept . of chem.engineering,colloge of engineering, university of Baghdad/iraq. E-mail: a.alnaama53@gmail.com*

drawbacks, among them, high cost and corrosion problems. Using heterogeneous catalysts will overcome these hadicaps. Solid acid-base catalyst could have many advantages like environmental, recycling, and separation. Bronsted acid-base sites and lewis acid-base sites have the activity to catalyze transesterification reaction **[10]**. **Amin and Anggoro [10]** investigated the activity and characterization of Cr, Cu, Ga impregnated ZSM-5 for conversion of methane to liquid hydrocarbon, they concluded that metal loaded HZSM-5 increases the activity of zeolite catalyst, Cr and Cu were selected for their roles as oxidizing and dehydrogenation agents.**Marchetti and Errazu [11]** studied the esterification reaction of oleic acid, using heterogeneous catalysts with different alcohols, they concluded that best conversion was with ethanol comparing with propanol and 2-propanol. **Lee,et al [12]** investigated the transesterfication in biodiesel synthesis, they concluded that the activity of the heterogeneous base catalyst could be increased to that of homogeneous catalyst by modifying the reaction conditions which are, the increasing the miscibility of oil-methanol by adding hydrocarbon co-solvent, using excess amount of alcohol, and solid catalyst-optimum amount.

2 Experimental

2.1 Zeolite preparation

Preparation of ZSM-5 zeolite samples were carried out in stainless steel autoclave lined with polytetraflouroethylene (PTFE). Tetraethylorthosilicate(TEOS-Sigma Aldrich) was used as silica source, aluminum isopropoxide (AIP-Sigma Aldrich) was used as alumina source, sodium hydroxide as alkaline agent, tetrapropyl ammonium hydroxide (TPAOH) as template, triethylenetetramine (Trien) as chelating agent, and deionized water as solvent. The template TPAOH (2.2 g) and TEOS (36 g) each were mixed with 40 ml deionized water for 1 h of stirring, then both were stirred and 1 ml ofTrien was added, then NaOH (2.05 g) dissolved in 40 ml was added also to make solution 1. AIP (0.82 g) was added to 40 ml deionized water and stirred for 1 h to make solution 2. Solution 2 was added to solution 1 drop wise with vigorous stirring (500 rpm) in mechanical stirrer for 2 h. The final gel was poured into a stainless steel autoclave lined with PTFE , the inside volume of PTFE insert is 200 ml and were filled up to 65% of its inside volume. The sealed autoclave was equipped with electric heating jacket and thermocouple with temperature and time controller, the autoclave is shown in Fig. 1. The crystallization reaction time and temperature to be set at 170 ^{o}C and 72 h. then the product was washed and filterred, dried at 100 ^{o}C, and calcined at 550 ^{o}C for 8 h. Preparation of ZSM-5/MCM-41 composite zeolite were carried using the ZSM-5 product from above, 2g of ZSM-5 zeolite was dispersed in 15 ml of a solution of sodium hydroxide (NaOH) 1.5 M and stirred for 1 h, then 3.75 g of cetyltrimethyl ammonium bromide (CTAB) to be dissolved in deionized water to get 10 wt.% aqueous solution and stirred for 30 min. The slurry solution of ZSM-5 in solution of NaOH was added to CTAB solution and adjust the pH value of reaction mixture to 10.5 by drop wise adding of 1M H_2SO_4 with vigorous stirring. The resulting mixture was transferred into the autoclave and operate the autoclave at 110 ^{o}C for 24 h. the autoclave then cooled down and adjust the pH of mixture to 8.5 by drop wise adding of 1M $H_2SO_4$with vigorous stirring, the autoclave was closed and operated again for 24 h and 110 ^{o}C at autogeneous pressure. The zeolite product then was washed and filtered, dried, calcined at 550 ^{o}C and 8 h.

Both prepared zeolites were wet impregnated with copper to get 15wt.% for Cu-ZSM-5 and 6-6 wt.% for Cu-Co-ZSM-5/MCM-41.

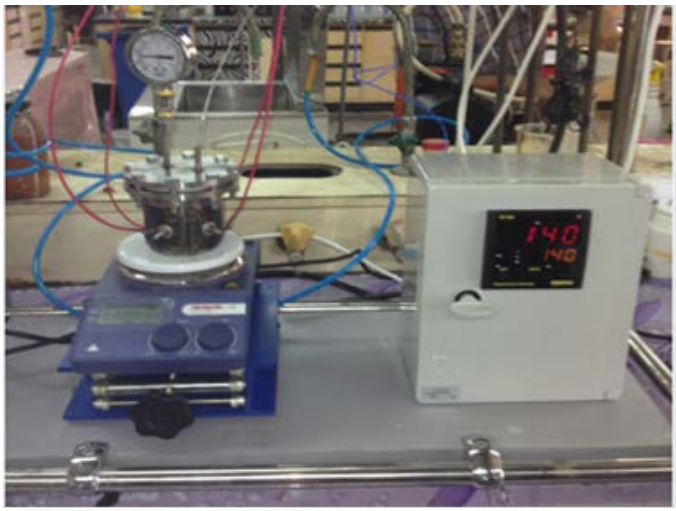


Fig.1 Autoclave Used in Zeolites Preparation

2.2 Biodiesel Production

Biodiesel production was carried out by semi-batch process, using oleic acid and ethanol. Using 0.52 g for catalyst weight which represent 2.5 wt. % relative to oleic acid. The glass assembly used for production of biodiesel is shown in fig.2

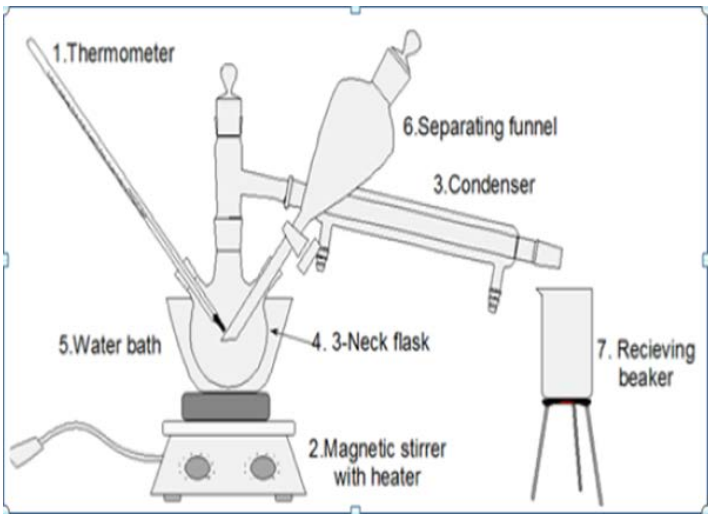


Fig.2 Glass Assembly for Semi-Batch Esterification

The technical procedure for the produced sample was to introduce 20.47g of oleic acid in the reactor, then heat to specified temperature, then the catalyst was added to the reactor and the alcohol in the separating funnel was opened to give a rate of 1 ml/s. the reaction will proceed and sample will be

drawn at each 30 s. the samples were produced at 50,60,70,and 80 °C.

Conversion was calculated by the following equation:

$$Conv.\% = \frac{acid\ no.of\ oleic\ acid - acid\ no.of\ sample}{acid\ no.of\ oleic\ acid}$$

Acid no. was estimated by titration of oleic acid and samples against 0.25 M solution of NaOH.

3 Results and Discussion

3.1 Characterization of Zeolite Figures and Tables

XRD patterns of ZSM-5 and ZSM-5/MCM-41 were determined using aD2 PHASER / Bruker (Germany 2010) using CuKα radiation Nickel filter (λ = 1.54Å). Data were collected within the 2θ range of 2° and 50° for ZSM-5 and range of 0° and 50° for ZSM-5/MCM-41, with a 0.02° 2θ-step and 0.5 s per step (30 kv and 10 mA). The X-ray patterns of ZSM-5 and ZSM-5/MCM-41 was implemented to check the required patterns and its crystallinity. Fourier transform infrared (FTIR) by Shimazdu-IRA AFFINITY-1, using KBr wafer 1 wt. % zeolite and 99 wt. % KBr to check and record the peaks at specified wave lengths corresponding to ZSM-5 and ZSM-5/MCM-41 in the range of 400-4000 cm^{-1}. The morphology of both kind of zeolites were studied by scanning electron microscopy using Te Scan, Vega III LM, CZECH. The particle size and topography on nano-level size were determined by atomic force microscopy, using an AA3300/Angstrom Advance Inc, USA, scanning probe microscopy (SPM) gave granularity cumulation distribution and surface roughness. Transmission electron microscopy (TEM) was implemented to study the morphology and texture, usingTEM Carl Zeiss-EM10C-100Kv-Germany. N_2 adsorption-desorption isotherms (BET) was implemented to determine BET surface and pore volume using BET Surface Analyzer Model 9600 series and Micrometrics ASAP 2020 Accelerated Surface area.

Fig. 3 and 4 shows the XRD pattern for ZSM-5 and ZSM-5/MCM-41 which they are both identical to typical ones, for ZSM-5, the typical peaks at 2θ = 7-9° and 23.5-24.5°. For ZSM-5 the peaks between 2-10° are typical and corresponding to reflections of hexagonal unit cell of MCM-41 zeolite crystal lattice.

Fourier transform infrared merged spectra for ZSM-5 zeolites and ZSM-5/MCM-41 are shown in figs 5 and 6. The findings for ZSM-5 FTIR spectra show that bands near: 1085 cm^{-1} is characteristic of internal asymmetric stretch vibration of Si-O-T external linkages, 546 cm^{-1} band for double five member ring (pentasil) vibration, and 452 cm^{-1} of T-O799 cm^{-1} is symmetric stretch of the bending vibration of SiO_4. All above mentioned bands are the evidence for formation of ZSM-5 and agree with results by **Amin &Anggoro [10].**

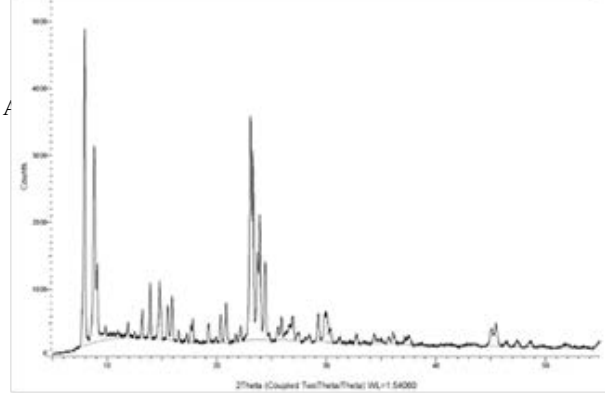


Fig.3 XRD pattern for ZSM-5 zeolite

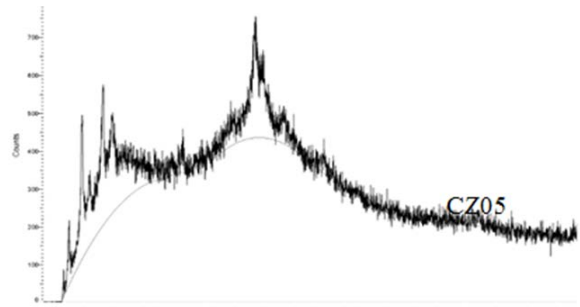


Fig.4 XRD Pattern for ZSM-5/MCM-41 composite zeolite

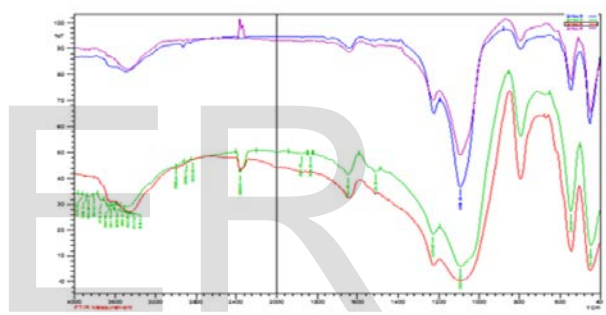


Fig. 5 FTIR Merged Spectra for samples ZSM-5 Prepared at 72h and 150(red),160(green).170(blue),and 180 °C(pink)

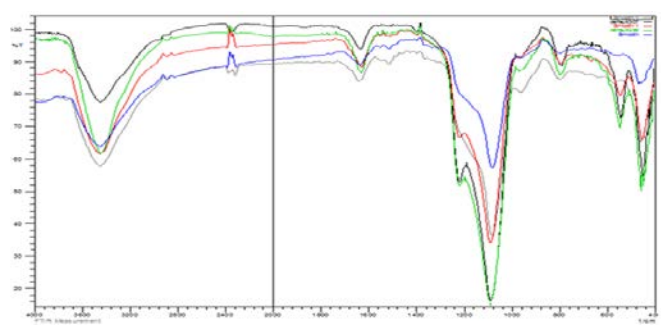
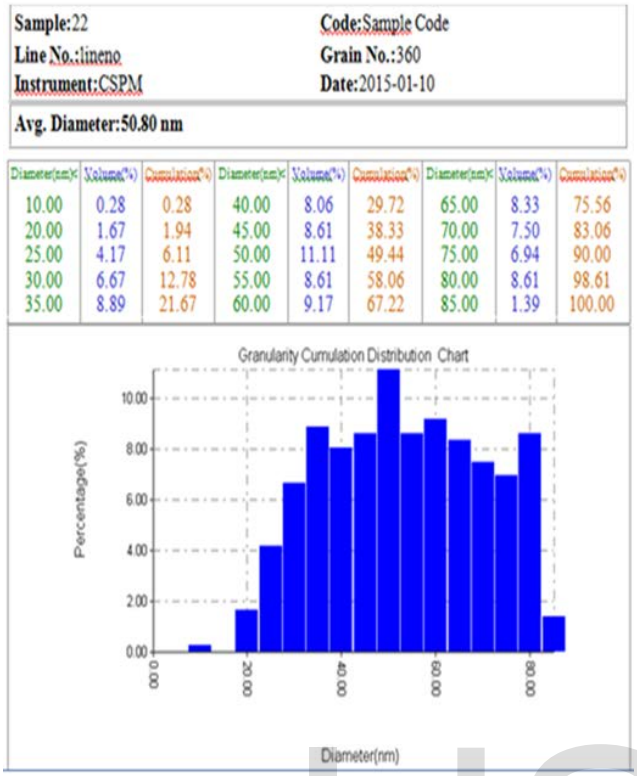


Fig.6 FTIR Merge Spectra for samples of ZSM-5/MCM-41

The particle size distribution and topography were investigated by atomic force spectroscopy were it gave average particle size of 50 nm, figure 7 shows the granularity cumulation distribution of particle size.



Sample:22 Code:Sample Code
Line No.:lineno Grain No.:360
Instrument:CSPM Date:2015-01-10
Avg. Diameter:50.80 nm

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
10.00	0.28	0.28	40.00	8.06	29.72	65.00	8.33	75.56
20.00	1.67	1.94	45.00	8.61	38.33	70.00	7.50	83.06
25.00	4.17	6.11	50.00	11.11	49.44	75.00	6.94	90.00
30.00	6.67	12.78	55.00	8.61	58.06	80.00	8.61	98.61
35.00	8.89	21.67	60.00	9.17	67.22	85.00	1.39	100.00

Fig.7 Granularity Cumulation Distribution for ZSM-5

The topography image for ZSM-5 in Fig.8 and Fig.9 showed the detailed observation of nano-scale events at crystal surface, showing also the layer growth of crystal and height of terraces. This finding are well agree with work of **Aghabozorg,et al [13]**.

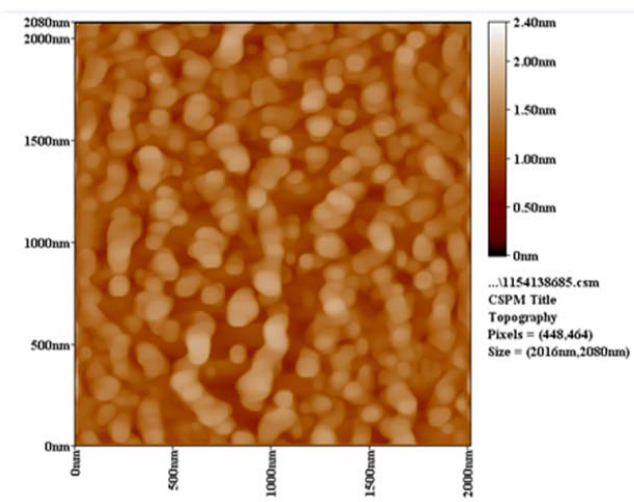


Fig. 8 AFM 2-Dimensional Image for ZSM-5

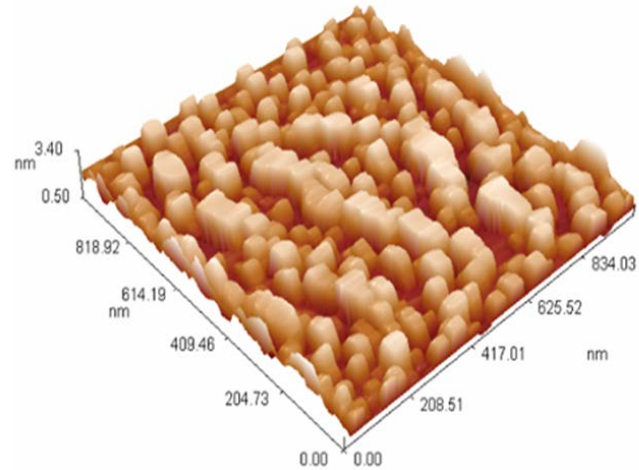
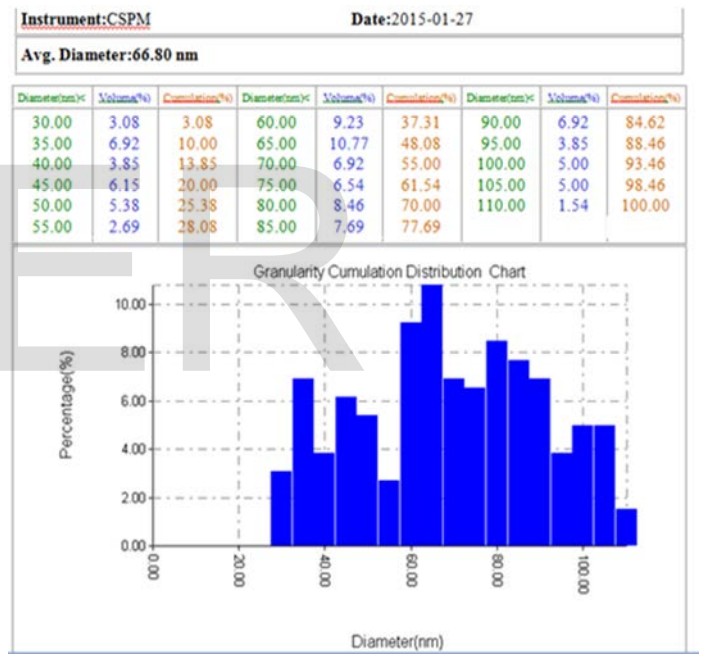


Fig. 9 AFM 3-Dimensional Image for ZSM-5

AFM report for ZSM-5/MCM-41 are shown in Fig. 10 for granularity cumulation distribution and show ave. diam.of 66.8 nm.Fig.11 shows AFM 2D



Instrument:CSPM Date:2015-01-27
Avg. Diameter:66.80 nm

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
30.00	3.08	3.08	60.00	9.23	37.31	90.00	6.92	84.62
35.00	6.92	10.00	65.00	10.77	48.08	95.00	3.85	88.46
40.00	3.85	13.85	70.00	6.92	55.00	100.00	5.00	93.46
45.00	6.15	20.00	75.00	6.54	61.54	105.00	5.00	98.46
50.00	5.38	25.38	80.00	8.46	70.00	110.00	1.54	100.00
55.00	2.69	28.08	85.00	7.69	77.69			

fig. 10 Granularity Cumulation Distribution for ZSM-5/MCM-41

Image,showing the nano-scale events at crystal surface, showing also the layer growth of crystal and height of terraces.

scanning electron microscopy images for ZSM-5 is shown in Fig.12

TEM image for loaded Cu-ZSM-5 are shown in Fig.13. It can be noticed the small dark circular spots which attributed to the metal loaded and distributed pretty well with mean diameter 7.414 nm as revealed by the histogram distribution of particle size, and this is an evidence that the metal loading was on nano-level size.

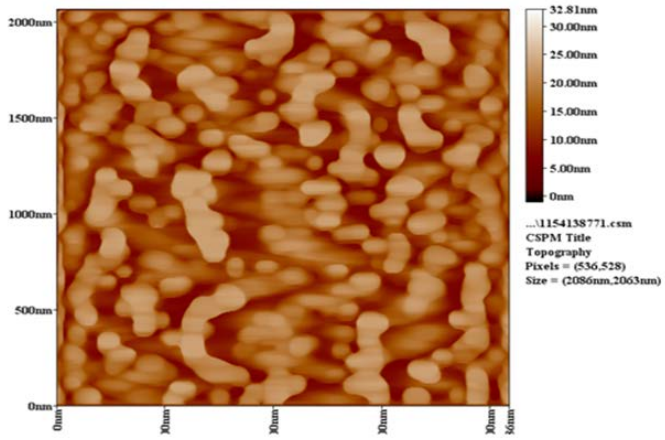


Fig. 11 AFM 2-Dimensional Image for ZSM-5/MCM-41

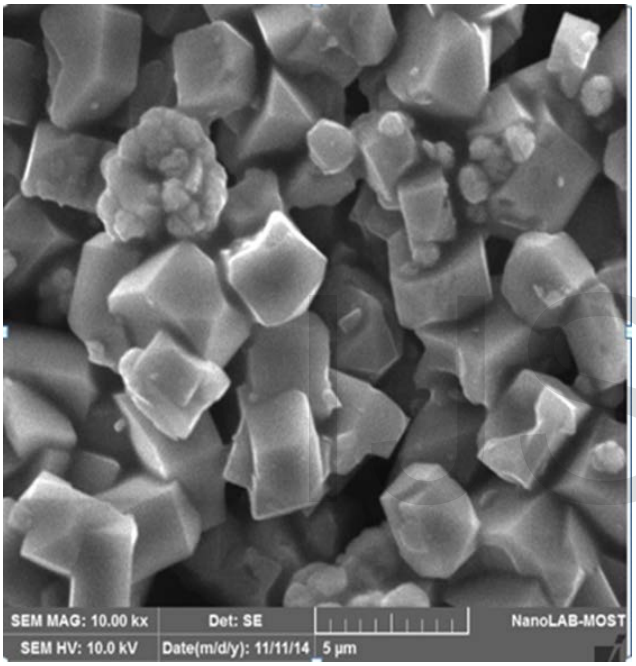


Fig. 12 SEM Image for ZSM-5

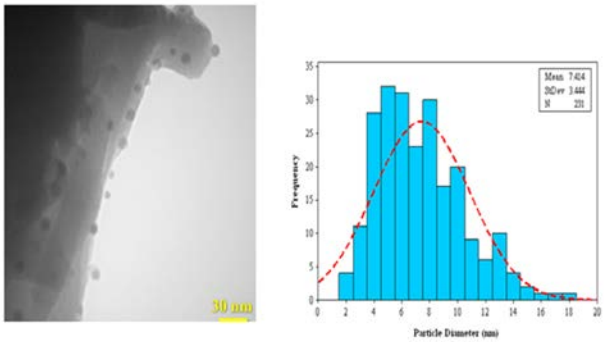


Fig.13 TEM image for Cu-ZSM-5 and Histogram Size Distribution of Metal loaded

TEM images for Cu-Co-ZSM-5/MCM-41 is shown in Fig. 14 with histogram distribution of particle size of bi-metal loaded.

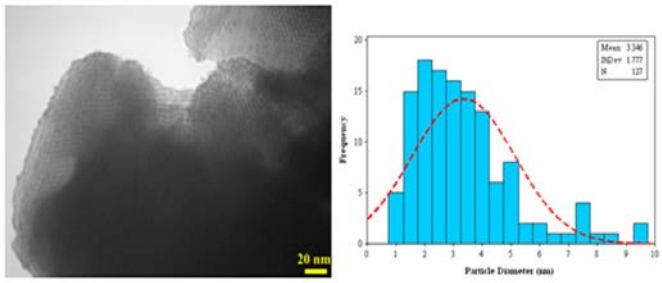


Fig.14 TEM Image for Cu-Co-ZSM-5/MCM-41 with Histogram Distribution of Size of the Loaded Bi-Metal

BET surface area of ZSM-5/MCM-41 were 612 m^2/g and with pore volume of 0.5421 cm^3/g.

3.2 Kinetics

Kinetics of esterification reaction of fatty acid (oleic acid) with ethanol, catalyzed by Cu-ZSM-5 and Cu-Co-ZSM-5/MCM-41 was investigated. The results as shown in Fig. 15 for the catalyst Cu-ZSM-5, a pseudo second order esterification reaction was found.

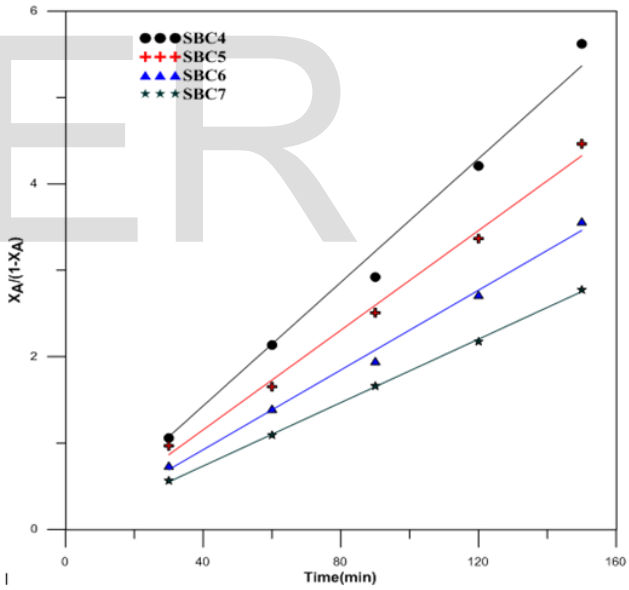


Fig.15 Second Order Esterification Reaction at various Temperature (50,60,70, and 80°C) for Semi-batch Process

For catalyst Cu-Co-ZSM-5/MCM-41 a pseudo second order was found also, as shown in fig. 16.

Estimation of activation energy gave 21.07 KJ/ mole for esterification with Cu-ZSM-5, and 19.5 KJ/mole with Cu-Co-ZSM-5/MCM-41.

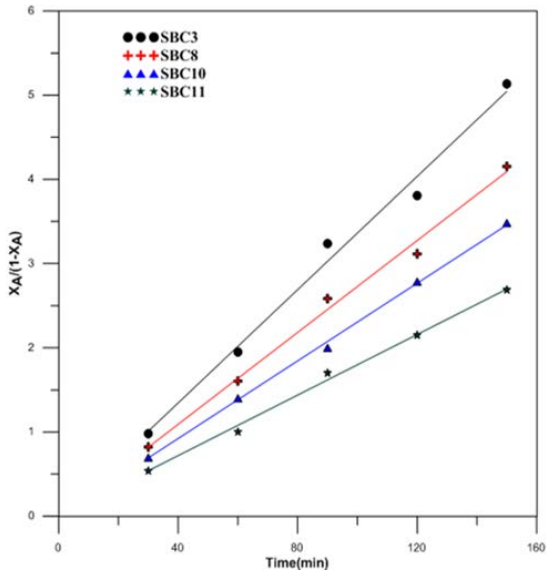


Fig.16 Second Order Esterification at various Temperature (50,60,70, and 80°C) for semi-batch Process

3.3 Conversions

Study of conversion between both types of catalysts, Cu-ZSM-5 and Cu-Co-ZSM-5/MCM-41, and comparing them with esterification without catalyst, fig.17 showed that Cu-ZSM-5 gave about 84.9% conversion and 83.5% for Cu-Co-ZSM-5/MCM-41, while gave 69% for without catalyst.

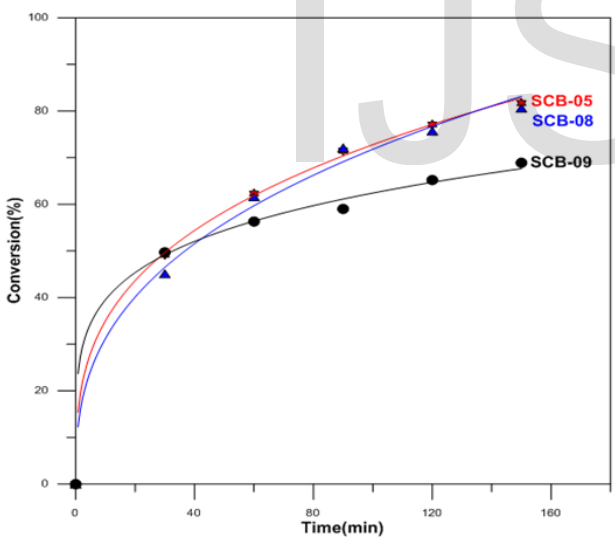


Fig. 17 Conversion in Heterogeneous Esterification with Two Types of Catalyst and without catalyst:SCB-9 without;SCB-5 with Cu-ZSM-5;SCB-8 with Cu-Co-ZSM-5/MCM-41

4 Conclusions

1. Nanocrystalline micro-mesoporous ZSM-5/MCM-41 composite zeolite was prepared successfully using alkaline leaching (treatment) method of ZSM-5 and two step crystallization. The optimum molarity of sodium hydroxide (NaOH) aqueous solution used is 1.5M, with CTAB (10 wt % solution) as surfactant and both gave best results.
2. Bimetal loading of cobalt and copper were conducted on ZSM-5/MCM-41 by wet incipient method successfully. TEM images revealed good distribution of metal oxide on zeolite surface with average diametet of 7.4 nm.
3. Semi-batch heterogeneous esterification gave good conversion of about 84.9 %, this conversion is attributed by shifting the reaction towards ester formation by excess of alcohol gradually added.
4. Extension of this work can be done by implementing semi-continuous heterogeneous esterification at elevated temperature above boiling temperature of water will eliminate water totally and shift the esterification reaction towards ester formation and increase in conversion can be reached.

Acknowledgment

The Author thanks chemical engineering department, college of engineering, university of Baghdad, for their support in conducting the research work in high study Lab., college of Science in conducting XRD, FTIR, and AFM. Also thanks are extending to Ministry of science and Technology for SEM test.

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