

## Synthesis and Characterization of Nanocrystalline Micro-Mesoporous ZSM-5/MCM-41 Composite Zeolite

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### Abstract

Nanocrystalline micro-mesoporous ZSM/MCM-41 composite was synthesized using alkaline treatment method and two step of crystallization in poly tetrafluoroethylene (PTFE) lined autoclave. The synthesized zeolites was characterized by X-Ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Atomic force microscopy (AFM), Fourier transport infrared (FTIR), and N<sub>2</sub> adsorption-desorption (BET). It was approved that the best results for alkaline leaching can be got with 1.5M NaOH solution. High surface (BET) area of 630 m<sup>2</sup>/g with pore volume of 0.55 cm<sup>3</sup>/g has been got. AFM reports showed a nano-level size for average particle size of 50nm.

**Key Words:** ZSM-5/MCM-41, Micro-Mesoporos, Nanocrystalline, Alkaline leaching, Composite molecular sieves.

### Introduction

The need of eco-friendly and more profitable and efficient technology for renewable sources of energy and fuel has encouraged and enhanced the potential to use and develop porous materials and especially micro-mesoporous composite molecular sieves. The goal of mesopore-modified zeolite is to create mesopores in zeolite to increase the accessibility to the internal surface. [1].

Micro-mesoporous composite zeolites have high specific surface area (BET) and pore volume.

The most disadvantage of zeolite is the small size of apertures (less than 0.8nm) and cavities less than 2nm, which imposes mass transfer problems because of diffusional limitations for

molecules and consequently on reactions which can cause back pressure on flow.

Overcoming these problems created by zeolite structure, several methodologies were adopted; among them are the synthesis of zeolite with larger pores and decreasing the zeolite down to nano-level size.

Comparing the dimensions of the zeolite micropores (< 2nm), mesopores (2-50nm) allow quicker transfer of reacting and produced molecules in the zeolite framework, and gives faster mass transfer of the reactants and products to and from the active sites.

The basic methodology to improve diffusion is to shorten the length of the micropore channels or/and to widen the pore diameter [2].

MCM-41 is one kind of mesoporous zeolite (molecular sieve) and exhibits a hexagonal arrangement, it has pore diameter ranging from 1.5 to 10nm, which gives much less transfer resistance comparing with ZSM-5. But the disadvantages of MCM-41 has nearly no acidity and poor hydrothermal stability. A combination of ZSM-5/MCM-41 could have a dual distribution of pore size, which would utilize the channel advantage of mesoporosity structure of MCM-41 with the thermal stability and several dual templating methods for preparation of mesoporous zeolite materials have been suggested like macrotemplating by using carbon black particles for synthesis of ZSM-5 having wide pore size distribution (10-100 nm), or using a nanocasting by colloid-imprinted carbons as templates for synthesis of ZSM-5 small particles [2].

**Jacobsen, et al.** [4] synthesized 12-30 nm mesoporous ZSM-5 by inserting the gel components with multiwall carbon nanotubes (MWCNT).

Leaching ZSM-5 with alkaline solution, sodium hydroxide (NaOH) was recently used to develop mesopores in MFI zeolite [5,6,7]. As it is well established that acid treatment eliminates framework Al atoms, alkali treatment was preferred to selectively eliminate framework Si atoms. It is also established and shown that mesopore formation is provoked at boundaries or defect sites of the zeolite crystals.

**Groen, et al.** [7] and **Groen, et al.** [8] studied the role of aluminum on the desilication process and gave a description for the mechanism of pore formation in MFI zeolites. In mole ratio  $\text{Si}/\text{Al} < 20$ , the presence of high Al concentrations inhibits Si from being eliminated, leading to limit pore formation. High  $\text{Si}/\text{Al}$  of  $\gg 50$ , show

excessive and unselective Si dissolution, and leads to create large pores. A ratio of  $\text{Si}/\text{Al}$  of 25-50 was established to be the optimum for development of mesoporosity with keeping Al atoms. The influence of the zeolite framework  $\text{Si}/\text{Al}$  ratio on Si extraction and the mechanism of porosity development are shown in Fig.1.

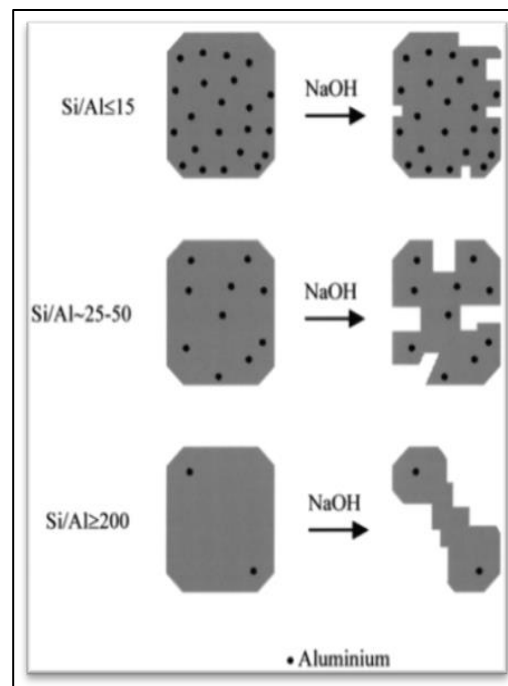


Fig. 1, Schematic Representation of the Effect of Content of Al on the Alkaline Leaching of MFI Zeolites [7]

The explanation of that was, for negatively charged  $\text{AlO}_4^-$  tetrahedron, hydrolysis of the Si-O-Al bond in the presence of  $\text{OH}^-$  is prevented compared to the relatively easy breakage of the Si-O-Si bond in the absence of neighbouring Al tetrahedral.

**Su, et al.**[9] By nuclear magnetic resonance (NMR) elucidated that the dissolution of the zeolite framework at Si-O-Si linkages. The inactivity of the Si-O-Al bond in alkali processing keeps the Bronsted acid sites (bridging OH species on Si-O-Al linkages).

Many different methodologies have been adopted to increase the accessibility in zeolites, one of them is to synthesis micro-mesoporous composite materials i.e. to synthesize materials which have larger pore and still have the catalytic ability of zeolites [3].

**Nam, et al.** [10] Investigated the synthesis of multiporous composite (MC-ZSM-5/MCM-41) by two steps, the first step was to prepare the ZSM-5 seeds by using Si-containing solution,  $Al(SO_4).18H_2O$ , template agent tetrapropylammonium bromide (TPABr) and sulfuric acid the mixture was stirred for 2h to get homogenous gel, then transferred into an autoclave at  $150\text{ }^\circ\text{C}$  for 10-15h to form ZSM-5 seeds. The second step, is to add cetyltrimethyl ammonium bromide (CTABr) to ZSM-5 zeolite seed with vigorous stirring at room temperature for 1h. The gel was transferred into autoclave at temperature  $150\text{ }^\circ\text{C}$  for 10-15h.

**Song, et al.**[3] Investigated the synthesis of MCM-41 composite from ZSM-5 zeolite, they used leaching by alkaline method, preparing first ZSM-5 zeolite ( $SiO_2/Al_2O_3$  ratio is 54) Then 5 g of ZSM-5 zeolite was added to 150 ml of a solution of sodium hydroxide (1M) and stirred for 1 h at 353 K. (2) prepare 10 wt.% Cetyltrimethylammonium bromide (CTAB). The (CTAB) solution was added to ZSM-5 alkalined suspended solution with stirring. The pH value was adjusted to 10.5 by drop wise addition of 2M  $H_2SO_4$  solution with vigorous solution. The solution mixture was then transferred into an autoclave and heated at 383 K for 48h at autoclave.

The results of XRD show that the samples synthesized have the ordered hexagonal mesoporous structure of

MCM-41-type molecular sieves. Also it shows that diffraction peak due to MFI-type framework of  $8\sim 10^\circ$ ,  $23\sim 25^\circ$  and  $45^\circ$ . The BET specific surface area was  $960\text{ m}^2/\text{g}$  with pore volume of 0.96 and  $0.24\text{ cm}^3/\text{g}$  for mesopores and micropores respectively.

**Tang, et al.** [11] Investigated the synthesis of micro-mesoporous ZSM-5/MCM-41 composite also used alkaline leaching method, by using different concentration of alkaline solution from 0.5 mol/l to 3.5 mol/l and 2.0 g ZSM-5 zeolite were alkalined with 10 ml NaOH at  $40\text{ }^\circ\text{C}$  for 1 h. ZSM-5 zeolite solution consisting of silicon aluminum fragments was formed. then 25ml of 10wt% of (CTAB) solution was added into the alkaline solution of ZSM-5 and stirred for 1h. The resulting solution was transferred in an autoclave with crystallization under  $110\text{ }^\circ\text{C}$  for 24 h.

A second crystallization step under same temperature and carried out after cooling the autoclave and adjusting the pH of the crystallization liquid to 8.5.

## Experimental

### 1- Materials

The materials used in preparation of ZSM-5 and composite ZSM-5/MCM-41 samples are shown in Table 1 below:

### 2- Procedure for Sample Preparation

ZSM-5 was prepared first [13], the template TPAOH (2.9g) and TEOS (36 g) were stirred (300 rpm) with (40 ml) deionized water in magnetic stirrer for 1h. Trien (1m) then was added, NaOH (2.05 g) dissolved in (40ml) deionized water was added also to make solution 1. Aluminum isopropoxide (AIP) 0.82 g was added to 40 ml deionized water and stirred for 1h to make solution 2.

The resulting mixture (solution 2) was added dropwise to solution 1 with vigorous stirring (500rpm) in mechanical stirrer for 2h. The resulting gel was poured into the autoclave, the inside volume of Teflon insert is 200ml and were filled to about 65% of its volume. A stir bar was placed inside the Teflon insert for stirring purpose. The autoclave then operated at 170° C and 72h.

The zeolite produced then washed by distilled water and filtered, then dried in oven at 100 °C for 24h. Calcination was done in electrical furnace at 550 °C and 8h, the temperature ramp was 1 °C/min The zeolite composition is as following (stoichiometric calculation):

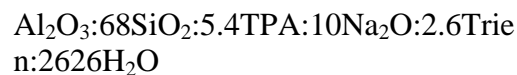


Table 1, Materials used in preparation of samples

No.	Material	Function	Formula	Company-supplier
1.	Tertaethylorthosilicate (TEOS)	Silica source	$\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$	Sigma Aldrich
2.	Cetyl trimethyl ammonium Bromide (CTAB)	Surfactant (Template)	$\text{C}_{19}\text{H}_{42}\text{BrN}$	Wuhan kemi-works,chemical Co.Ltd.
3.	Aluminum isopropoxide(AIP)	Alumina source	$\text{C}_9\text{H}_{21}\text{AlO}_3$	Sigma Aldrich
4.	Tetrapropyl ammonium hydroxide( TPAOH)	Template (OSDA)	$\text{C}_{12}\text{H}_{28}\text{NOH}$	Wuhan kemi-works chemical Co.,Ltd.
5.	Sodium hydroxide	Mineralizer (Alkaline agent)	NaOH	Sigma Aldrich
6.	Triethylenetetramine (TRIE N)	Chelating agent	$\text{NH}_2\text{CH}_2\text{CH}_2(\text{NHCH}_2\text{CH}_2)_2\text{NH}_2$	Fluke AG



Fig. 2, Twin Autoclave Lined with PTFE

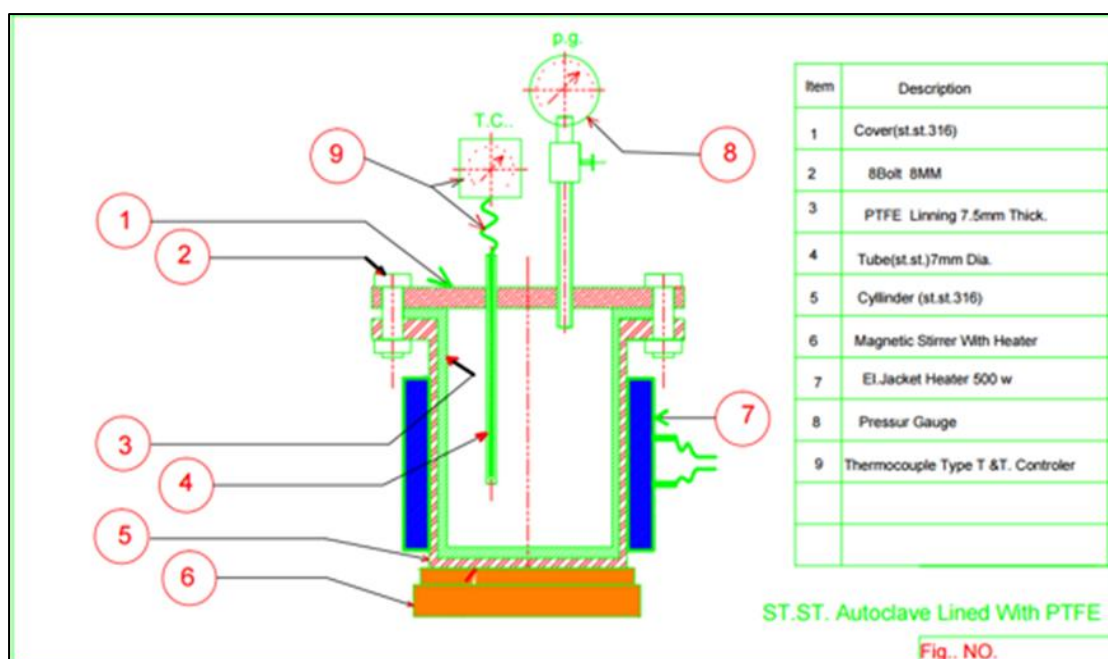


Fig. 3, Design of the Autoclave Lined with PTFE

ZSM-5/MCM-41 samples were prepared as following:

- 1- 2g of ZSM-5 prepared above was dispersed in 15 ml of a solution of sodium hydroxide (NaOH) and stirred for 1h at 40° C, different molarity for sodium hydroxide aqueous solution were used (1.5M, 2.0M, 2.5M).
- 2- 3.75g of cetyltrimethyl ammonium bromideto be dissolved in deionized water to get 10 wt. % aqueous solutions and stirred for 30min.
- 3- The obtained slurry solution in (1) was added to (CTAB) solution in (2) and adjust the pH value of reaction mixture to 10.5 by adding drop wise of 1M H<sub>2</sub>SO<sub>4</sub> solution with vigorous stirring for 1h.
- 4- The reaction mixture in (3) was transferred into the autoclave lined

with PTFE as shown in Figure 1 and operates at 110° C for 24h.

- 5- Cool the autoclave and adjust the pH of mixture to 8.5 by drop wise adding of 1M H<sub>2</sub>SO<sub>4</sub> with vigorous stirring.
- 6- Close and operate the autoclave again for second step of crystallization at 110° C and 24h.
- 7- The zeolite product then washed, filtered, and dried in oven at 100° C for 24h, then calcined at 550° C and 8h.
- 8- Bi-metal loading for the synthesized zeolite was done by wet incipient impregnation method; the percentage of loading was 6 wt. % for copper and 6 wt. % for cobalt.

The samples of ZSM-5/MCM-41 prepared are shown in Table 1.

Table 2, Samples Conditions for Composite ZSM-5/MCM-41

No.	Sample code	Weight of zeolite,g	Volume of CTAB solution (10wt %) ml	Molarity of alkaline solution , M	Volume of alkaline solution,ml	Crystallization (2 step) temperature °C/time,h
1.	CZ-01	2	37.5	1.5 M	15	110C/24h
2.	CZ-02	2	37.5	1.5 M	15	110C/24h
3.	CZ-03	2	37.5	1.5 M	15	110C/24h
4.	CZ-04	2	37.5	1.5 M	15	110C/24h
5.	CZ-05	2	37.5	2.0 M	15	110C/24h
6.	CZ-06	2	37.5	2.5 M	15	110C/24h
7.	CZ-07	5	62.5	1.5 M	25	110C/24h



## Characterization

The XRD patterns of ZSM-5 and ZSM-5/MCM-41 zeolites were determined using instrument D2 PHASER/Bruker (Germany 2010) using CuK $\alpha$  radiation Nickel filter ( $\lambda=1.54\text{\AA}$ ). Data were collected within  $2\theta$  41, with a  $0.02^\circ$   $2\theta$ -step and 0.5s per step, 30Kv and 10mA X-ray was Transform Infrared (FTIR) by Shimadzu-IRA, AFFINITY-1, using KBr wafer 1wt. % zeolite and 99wt.% KBr to check and record the peaks at specified wave lengths corresponding to ZSM-5/MCM-41 and in the range of  $400\text{-}4000\text{ cm}^{-1}$ . The morphology of composite ZSM-5/MCM-41 was

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 AA3000/Angstrom Advance Inc, USA. Adsorption-desorption N<sub>2</sub> BET surface was measured by surface analyzer/Q surf series/Italy and ASAP 2020/USA. The structure of synthesized nanocrystalline samples were investigated by transmission electron microscopy by Carl Ziess-EM10C-100Kv-Germany instrument.

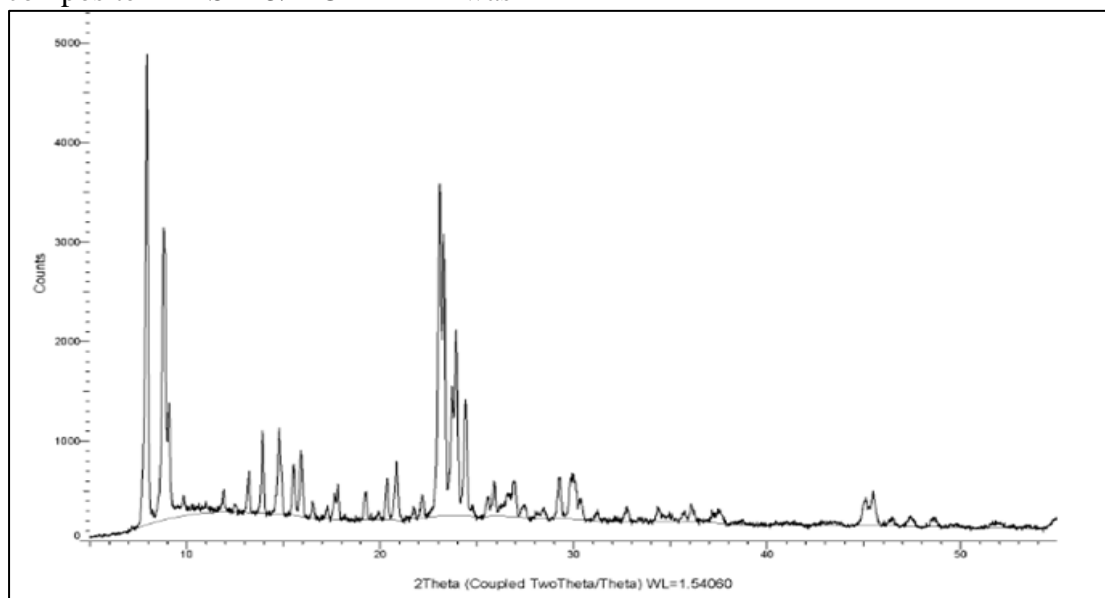


Fig.4, XRD Pattern for Prepared Sample of ZSM-5 Zeolite

## Results and Discussion

### 1- X-Ray Diffraction

The XRD-pattern of prepared sample of ZSM-5 was examined, and showed that the only phase obtained was for ZSM-5, the peaks at  $2\theta$  ranges of 7-9 $^\circ$  and 22.5-24.5 $^\circ$  are identical to the theory and typical [14]. Figure 3 show the pattern for prepared ZSM-5 zeolite, the typical peaks are well appeared in the pattern. The results of XRD patterns of nanocrystalline micro-mesoporous ZSM-5/MCM-41 are

shown in Figure 4 for samples CZ01, CZ05, and CZ06. The molarity of alkaline (NaOH) solution were 1.5M, 2.0M, and 2.5M respectively. The difference in crystallinity is clearly shown because of the effect of increasing alkalinity which cause the dissolution and desilication of silica by alkaline leaching led to increased loss in ZSM-5 phase. The results also showed that samples prepared have the ordered hexagonal mesopores structure of MCM-41 zeolite, and was observed

in the peaks at  $2\theta = 2-10^\circ$ , and they are typical, Figure 4 showed these facts.

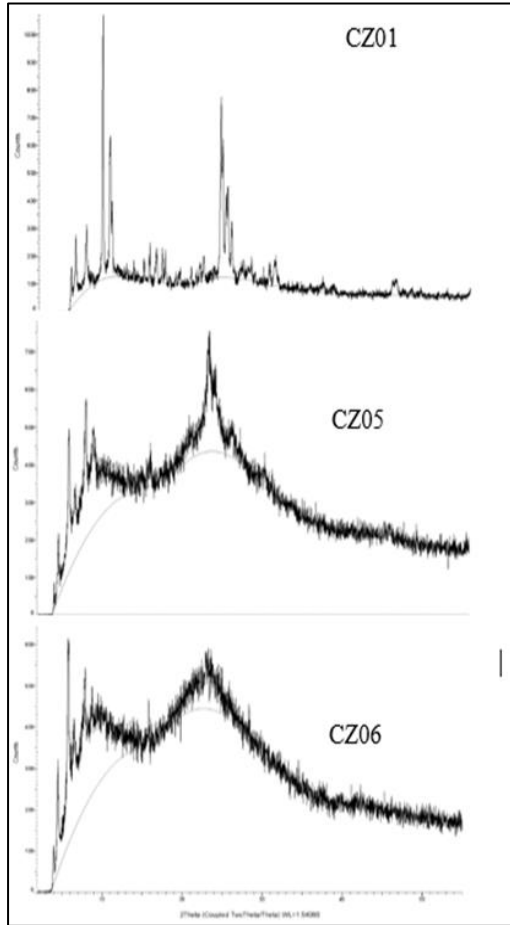


Fig. 5, XRD Patterns for samples CZ01, CZ05, and CZ06 Alkaline Leached 1.5, 2, 2.5M respectively

**2- Atomic Force microscopy (AFM)**

The particle size distribution and topography was investigated by atomic force microscopy, with different topography pixels (536-528). AFM images for 2 and 3-dimensional surface profiles showed the detailed observation of nanometer size events and the layer growth of crystals of zeolite, and as shown in figures 5 and 6.

Granularity cumulation distribution reports showed that a nano-size level has been got for ZSM-5/MCM-41 zeolite down to 56.7 nm, as shown in Figure 7 below:

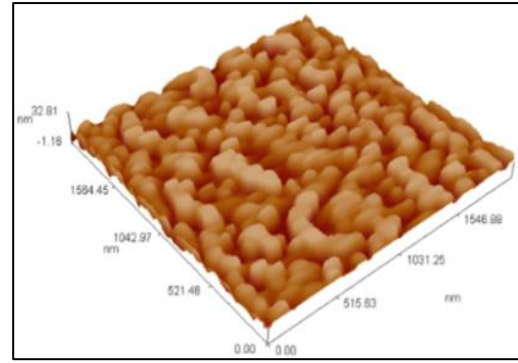


Fig. 6, AFM 3-Dimensional Image for Sample CZ01

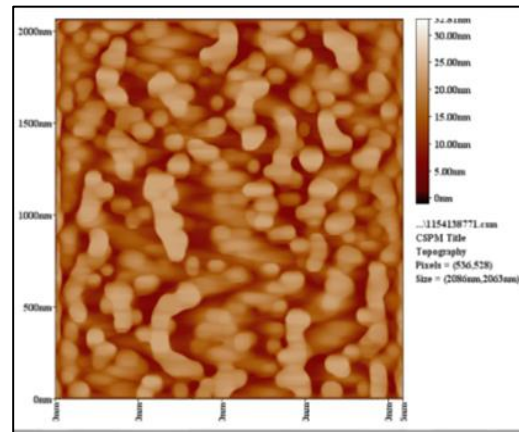


Fig. 7, AFM 2-Dimensional Image for Sample CZ01

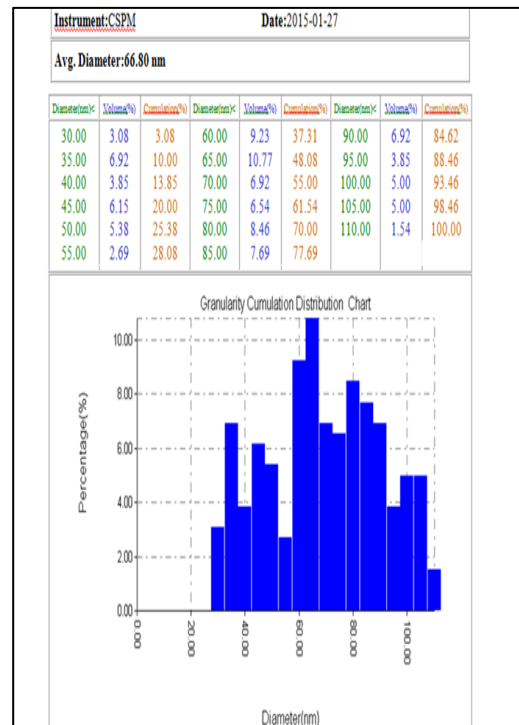


Fig. 8, Granularity Cumulation Distribution Chart for Sample CZ01

In Table 3 showed the particle size and distribution range for all samples of ZSM-5/MCM-41.

Table 3, Particle Size and Distribution Range for Prepared Samples

Sample	Ave. particle diam., nm	Range of particles distribution, nm
CZ-01	66.8	30-110
CZ-02	N.M	N.M
CZ-03	62.8	40-80
CZ-04	58.5	35-80
CZ-05	72.7	60-100
CZ-06	77.1	55-105
CZ-07	56.7	40-100

### 3- Surface area and Pore Volume

The micro-mesoporous ZSM-5/MCM-41 showed an increase in BET

Table 4, Parameters Results for prepared Samples of ZSM-5/MCM-41

Sample	Ave. particle diam, nm	S.surface(BET), m <sup>2</sup> /g	Pore volume, cm <sup>3</sup> /g	Crystallinity %
CZ-01	66.8	630	0.5449	76.2
CZ-02	N.M.(not measured)	490	0.4338	64.7
CZ-03	62.8	537	0.5414	107.5
CZ-04	58.5	707.7	0.6482	101.7
CZ-05	72.7	1030.9	0.8362	85.2
CZ-06	77.1	923.2	0.7769	50.8
CZ-07	56.77	575.9	0.434	94.2

### 4- Fourier Transport Infrared (FTIR)

The figure 9 for prepared samples of micro-mesoporous ZSM-5/MCM-41, showed that there are small shift in band near 1100 cm<sup>-1</sup> to slightly decreased as the treatment of alkaline solution increased from 1.5M (NaOH) for CZ01 (black line), CZ03 (red line), CZ04 (green line) to 2.0M (NaOH) for CZ05 (blue line), then to 2.5M for CZ06 (grey line).

surface and pore volume, and the best results were given by samples CZ01, CZ03, CZ04, CZ07, which they were alkaline leached by 1.5M (NaOH solution). The results as mentioned in Table 4 below, the average BET surface and pore volume of above mentioned samples are 612 m<sup>2</sup>/g and 0.5421 cm<sup>3</sup>/g respectively. From Figure 8 for N<sub>2</sub> adsorption-desorption isotherm, it is clearly shown that the material has mesopore and micropore characteristics. At a relative pressure < 0.3 the increase in the amount adsorbed corresponds to the filling of micropores and little bit of mesopores in ZSM-5. At relative pressure range from 0.3-0.5 a rise of sorption which indicates the presence of mesopores. It showed a type I hysteresis loop at relative pressure range 0.85-1.00. This finding is well matched with previous works [3, 12, and 18].

The gradual shifting of the band at 1100 cm<sup>-1</sup> towards slightly lower wave number, accompanied with a decrease of the band near 440-450 cm<sup>-1</sup>. This show and indicate formation of amorphous silica on the surface of ZSM-5 [15, 16], and coincided with previous work [17].



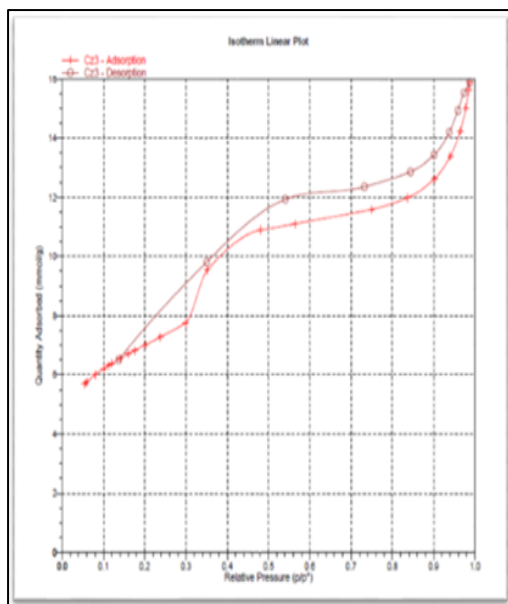


Fig .9, Isotherm Plot for ZSM-5/MCM-41, Sample CZ03

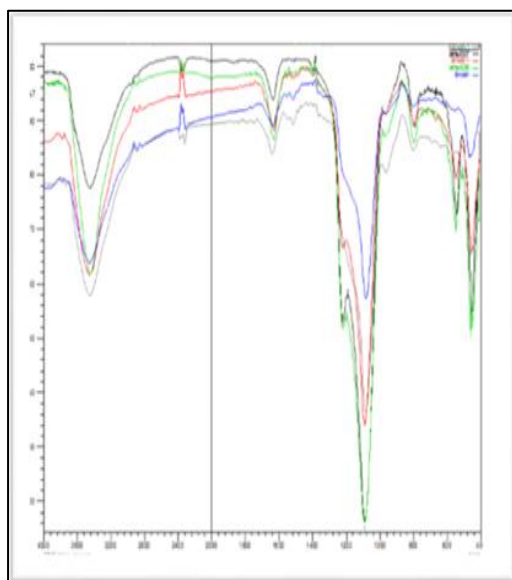


Fig. 10, FTIR Spectra (Merge) for samples CZ01, CZ03, CZ04, CZ05, and CZ06

### 5- Scanning Electron Microscopy

SEM images for composite ZSM-5/MCM-41 are shown in fig.10. It is clearly revealed that some of ZSM-5 crystals are subjected to some faults and cracks on the surface of ZSM-5 particles because of de-agglomeration of crystals, which is a consequence of alkali treatment and cleavage of intracrystalline Si-O-Si bonds.

These cracks increase with the increase of the duration and molarity of alkali treatment. This finding is well matched with the previous works [11, 17].

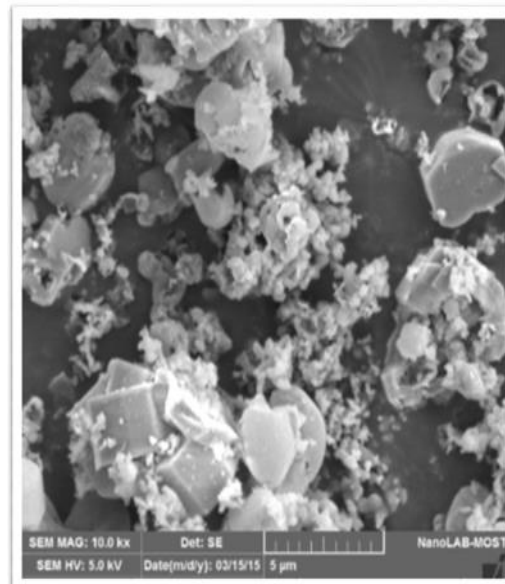


Fig. 11, Scanning Electron Microstructure Image for ZSM-5/MCM-41, Sample CZ01

### 6- Transmission Electron Microscopy

The structure of synthesized nanocrystalline samples of ZSM-5/MCM-41 were investigated by transmission electron microscopy.

TEM images are shown in fig.11 and fig.12, for composite zeolite loaded with copper and cobalt. It can be indicated the well-ordered hexagonal arrays of mesopores structure of MCM-41 which are interconnected with framework of ZSM-5. The small circular shape and dark spots are for the loaded copper and cobalt oxides and have mean diameter 3.346nm as shown in histogram size distribution. These images are well agreed with previous works [3, 10].

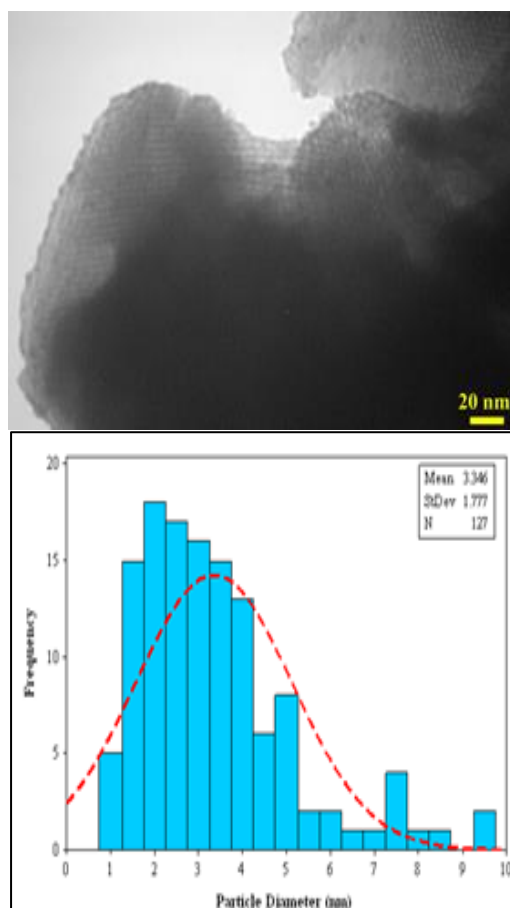


Fig. 12, TEM Image for Cu-Co-ZSM-5/MCM-41 with Histogram Size Distribution

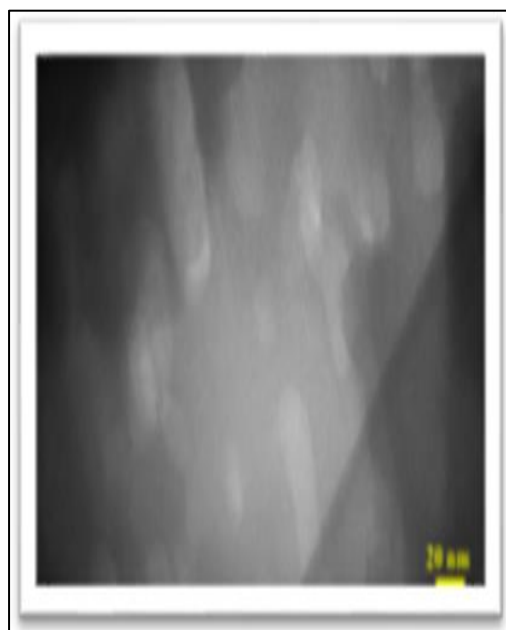


Fig. 13, TEM Image for Cu-Co-ZSM-5/MCM-41

## 7- Alkaline Treatment

Alkaline treatment method for getting mesoporosity proved to be a successful method to combine two types of zeolite in which their physical and catalytic properties are complementary for each other, in other words it combines the mesoporosity of MCM-41 and acidity of ZSM-5. The best concentration of alkaline solution of 1.5M in which best characteristics got concerning BET surface, pore volume, crystallinity, as mentioned in table 4, and nano-size level. Surfactant or second template, CTAB gave promising results in two step crystallization process to get composite zeolite, and when comparing typical isotherms shown by Na et al.,[18] with synthesized sample CZ01 reveal that the sample CZ01 synthesized with C19 (Cetyl trimethyl ammonium bromide-CTAB-C<sub>19</sub>H<sub>42</sub>BrN), showing that pores in this system can be controlled by varying the chain length of alkyl methyl ammonium surfactant. pH control during the preparation procedure play a vital role in getting best result.

## Conclusions

- 1- Nanocrystalline micro-mesoporous ZSM-5/MCM-41 composite zeolite can be synthesized successfully by alkaline treatment of ZSM-5 followed by thermal treatment-conventional method using two step crystallization and CTAB as second template.
- 2- XRD-patterns, of prepared samples of composite ZSM-5/MCM-41 zeolite showed excellent agreement with typical pattern and theory.
- 3- The optimum concentration of alkaline (NaOH) solution is 1.5M , giving best characteristics results.
- 4- Atomic force microscopy reports revealed nano-level size for average particle size.

5- Bi-metal loading of copper and cobalt were conducted on ZSM-5/MCM-41 by wet incipient impregnation method. TEM images revealed good distribution of metal with average diameter of 3.346 nm.

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