

## FULL LENGTH ARTICLE

# Synthesis, Characterization and Catalytic Activity of Zeolites

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### ABSTRACT

MCM 41 zeolite has been synthesized by hydrothermal method in an autoclave. For, comparison a few other zeolite as Y-zeolite,  $\beta$ -zeolite and zsm-5 have been procured from commercial sources. The zeolites were characterized by techniques such as powder X-ray diffraction (PXRD), n-butyl amine back titration method and Infrared spectroscopy (FTIR) for their crystalline nature, total acidity and the surface functional groups respectively. The surface properties were correlated with their catalytic activity by conducting test reactions such as esterification reaction and dehydrogenation reaction in liquid and vapour phase respectively.

**Keywords**— Zeolites, catalytic activity, composite materials, nanocomposites.

### INTRODUCTION

The word catalysis (katalyse) was coined by [1] "Catalysts are substances which by their mere presence evoke chemical reactions that would not otherwise take place." The idea of catalysis extends far back into chemical history. Wilhelm Ostwald was the first to emphasize that a catalyst influences the rate of a chemical reaction but has no effect on the position of equilibrium. His famous definition was, "a catalyst is a substance that changes the velocity of a chemical reaction without itself appearing in the end products." One should differentiate catalytic materials from catalysts. The former are substances that simply display some catalytic activity. The latter are substances (some of which are items of commerce) that can be used in chemical processes [2].

A catalysis scientist looks mainly for the following basic information.

- *Activity of catalyst*: High activity for fast reaction rate and a short reaction time to maximize production throughput.
- *Selectivity of catalyst*: High selectivity means to maximize the yield, to eliminate by-products and reduce purification costs.
- *Stability of catalyst*: High thermal and mechanical stability over the reaction temperature [3].
- *Reusability*: High recycle capability and minimum costs.
- *Fast filtration rate*: Rapid separation of the catalysts and the final product, ensuring maximum production rates.

Heterogeneous catalyst has been given much attention to overcome the problems. Solid catalysts such as zeolites [4-5], phosphotungstic acid ( $H_3PW_{12}O_{40}$ ) supported on  $SiO_2$  in the form of Cerium salt [6], mesoporous molecular sieves such as MCM-41 [7] and clay such as montmorillonite [8] are among the solid acid catalysts that have been used in Cannizzaro reaction.

The use of above mentioned liquid catalysts is undesirable from the environmental point of view as these chemicals are corrosive and generally encounter the problems of handling and transportation. Moreover, high product selectivity and reusability of the catalysts cannot be expected [9].

### EXPERIMENTAL METHODS

#### A. PREPARATION OF THE CATALYST MCM-41

2.4 g of n-Cetyl Trimethyl Ammonium Bromide (CTAB) was dissolved in 120 g of distilled water and stirred until the solution was homogenous and clear. After the addition of 8 ml of ammonium hydroxide, the mixture was stirred for 5 min and then 10 ml of Tetra Ethyl Ortho Silicate (TEOS) were added [10].

The molar composition of the gel was 1M TEOS: 1.64 M: NH<sub>4</sub>OH:0.15 CTAB: 126 M H<sub>2</sub>O. The reactions were stirred overnight. The solid obtained was filtered and washed consecutively with water and methanol. Calcinations were performed at 823 K for 5h.

#### B. N-BUTYLAMINE BACK TITRATION METHOD

Take 0.1 g of the zeolites add to 10 ml of 0.05M n-butylamine. Keep the flask aside overnight (closed). Next day take 5 ml of the supernatant n-butylamine and titrate it against 0.05M HCl using 0.2% bromothymol blue indicator. The surface acidity is calculated from the decrease in the concentration of n-butylamine when a known weight of a catalyst with a known volume of n-butylamine of known concentration.

### CATALYTIC STUDIES

#### LIQUID PHASE ESTERIFICATION REACTION

Take 10 ml each of 1 M glacial acetic acid and ethyl alcohol in 100 ml round bottom flask. Fit it with a clean water cooled condenser. Add 0.1 g of sample along with the solution. Reflux for 1 hour on a mantle /oil bath at 50°C. After this time, cool the reaction mixture. Filter the catalyst and titrate it against 2 M standard NaOH solution. The difference in the titre value of NaOH before and after the reaction corresponds to the amount of ester formed [11, 12, and 13].

#### VAPOUR PHASE DEHYDROGENATION REACTION.

The apparatus is flushed with nitrogen for 10 minutes at the beginning of every run to obtain an inert atmosphere. The reactant is fed into the reactor by means of motor driven syringe for accurate control metering flow rate. The reactor containing the catalyst is kept inside the furnace which is electrically. The temperature of the furnace was controlled by on-off temperature controller-cum indicator within +/-20°C [14].

The effluent stream from the reactor is cooled by means of water condenser and the liquid products are collected in trap which is cooled with ice cold water. The gaseous products are collected in a burette. The time for which the reactant would be in contact with catalyst is expressed as the time taken for the flow of the volume of the reactant equivalent to the volume of catalyst at a particular temperature. The contact is given by the following equation: contact time =  $3600V_c / V_r$  second where  $V_c$  is the volume of the catalyst and  $V_r$  volume of the reactor. The duration of each experiment was 1 to 1.5 hr.

### RESULTS AND DISCUSSIONS

The objectives of the work are synthesis of MCM-41 by hydrothermal process followed by characterization and to study the catalytic activity of MCM-41 and other zeolites brought commercially viz Y-zeolite,  $\beta$ -zeolite and ZSM-5. The catalytic activity involved the liquid phase esterification and vapour phase dehydrogenation reaction.

#### SYNTHESIS OF MCM-41

MCM-41 can be synthesized by various procedures. However, hydrothermal method was suitably used for the production of the catalyst.

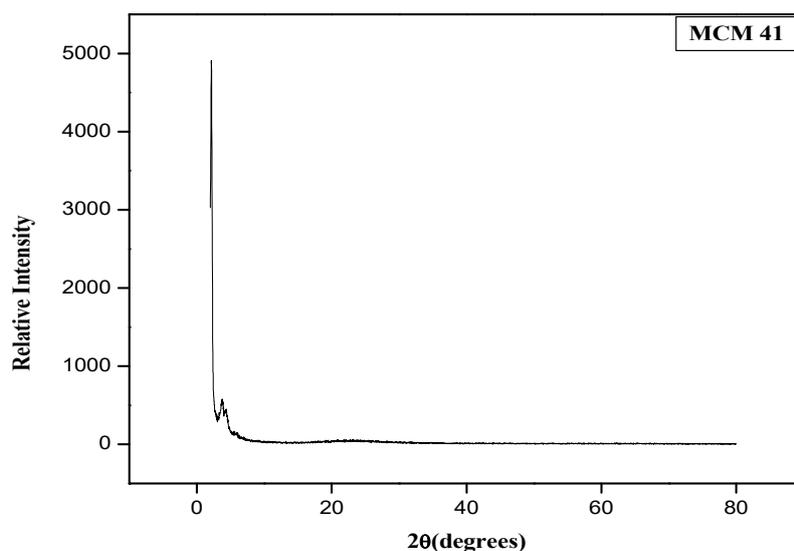


Fig: 1 XRD pattern of MCM-41

The XRD patterns of MCM-41 given in the figure 1 exhibit single reflection at  $2\theta = 2.11^\circ$ . Clearly indicates the MCM-41 phase. The weak reflection observed at  $2\theta = 4.06^\circ$  indicates the less long range powder of the material.

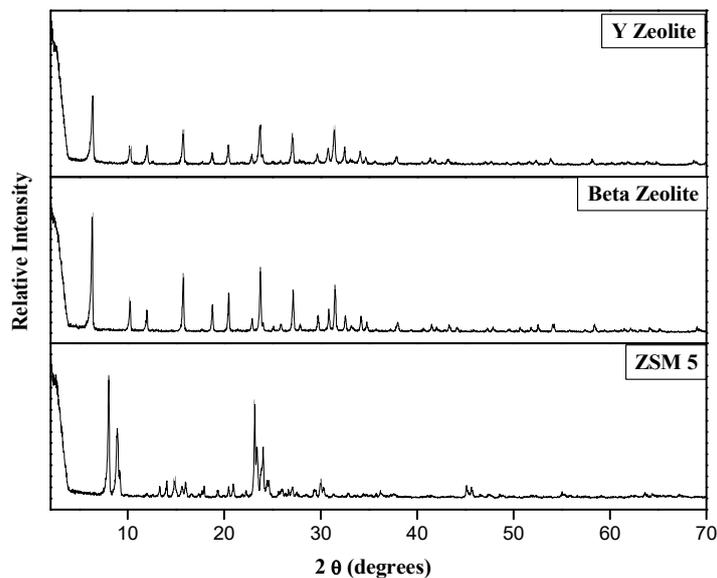


Fig: 2 PXR D pattern of Y-zeolite,  $\beta$ -zeolite and ZSM-5

The weak intensities observed in the XRD pattern of the material given in the figure 2 can be inferred that this material may consists of micro crystalline zeolite solids. The high intensities peak at  $2\theta = 2-3^\circ$  is a characteristic of mesoporous materials.

#### INFRARED STUDIES

The Infrared region useful for the zeolite characterization is mainly the mid-IR region ( $140\text{ cm}^{-1}$ - $300\text{ cm}^{-1}$ ). Since this region contains fundamental vibration (rotational-vibrational) of the frame work silica-alumina tetrahedral.

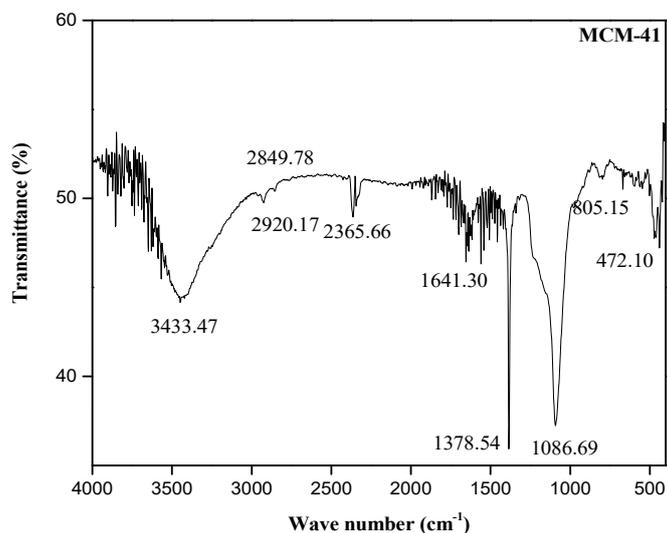
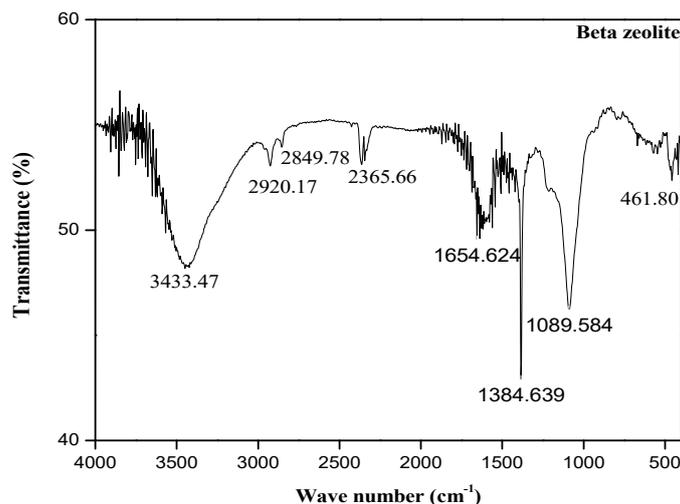


Fig: 3 IR pattern of MCM-41

The absorption band in the figure 3 at  $1086.69$ ,  $805$ ,  $472\text{ cm}^{-1}$  have been assigned to the asymmetric stretching and bending modes of  $\text{Si}(\text{Al})_4$  tetrahedral. The broad band at  $3433.47$  is due to the presence of stretching vibration of hydrogen bonds as hydroxyl group. These hydroxyl groups are due to the absorption of water which is a characteristic of mesoporous material. The appearance of broad band at  $1641.30$  is due to the stretching vibration of hydroxyl group. The vibration band at  $1086.69\text{ cm}^{-1}$  is for the pure siliceous compounds.

Fig 4: IR pattern of  $\beta$ -zeolite

The absorption band in the figure 4 at 1089.58, 811.27, 461.80 cm<sup>-1</sup> have been assigned to the asymmetric stretching and bending modes of Si (Al)<sub>4</sub> tetrahedral. The broad band at 3433.47 is due to the presence of stretching vibration of hydrogen bonds ay hydroxyl group [15]. These hydroxyl groups are due to the absorption of water which is a characteristic of mesoporous material. The appearance of broad band at 1654.624 is due to the stretching vibration of hydroxyl group. The vibration band at 1089 cm<sup>-1</sup> is for the pure siliceous compounds.

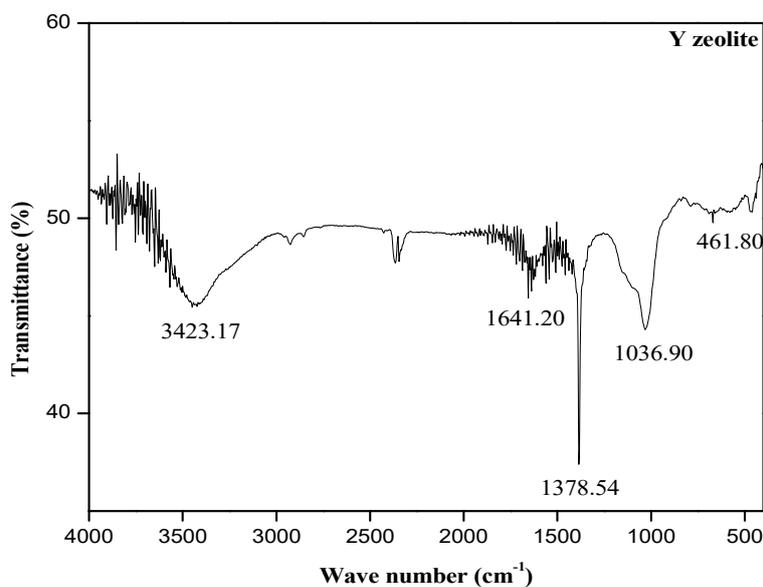


Fig 5: IR pattern of Y zeolite

The absorption band in the figure 5 at 1378.54, 1036.90, 461.80 cm<sup>-1</sup> have been assigned to the asymmetric stretching and bending modes of Si(Al)<sub>4</sub> tetrahedral. The broad band at 3423.17 is due to the presence of stretching vibration of hydrogen bonds ay hydroxyl group. These hydroxyl groups are due to the absorption of water which is a characteristic of mesoporous material. The appearance of broad band at 1641.20 is due to the stretching vibration of hydroxyl group. The vibration band at 1036.90cm<sup>-1</sup> is for the pure siliceous compounds.

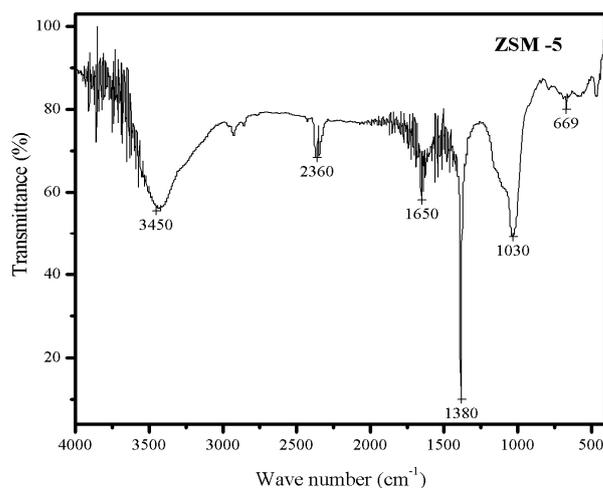


Fig 6: IR pattern of ZSM-5

The absorption band in the figure 6 at 1380, 1030, 669  $\text{cm}^{-1}$  have been assigned to the asymmetric stretching and bending modes of  $\text{Si}(\text{Al})_4$  tetrahedral. The broad band at 3450 is due to the presence of stretching vibration of hydrogen bonds by hydroxyl group. These hydroxyl groups are due to the absorption of water which is a characteristic of mesoporous material. The appearance of broad band at 1650 is due to the stretching vibration of hydroxyl group. The vibration band at 1030  $\text{cm}^{-1}$  is for the pure siliceous compounds

## CONCLUSIONS

The synthesis of MCM-41 was done by hydrothermal method. For comparison three more zeolites were purchased commercially viz Y-Zeolite,  $\beta$ -Zeolite and ZSM-5. Characterization of the samples was done by PXRD for crystallinity, n-butylamine test for surface acidity and FTIR for surface functional groups.

The results of all the samples were accordance to the literature. MCM-41 has shown the least acidity and IR has shown its hydroxyl group. The surface acidity varied in the following order  $\beta$ -Zeolite>Y-Zeolite >ZSM-5 >MCM-41.

Liquid phase esterification reaction and vapour phase dehydrogenation reaction was carried out to find out the catalytic activity of the samples.  $\beta$ -Zeolite has shown the best catalytic activity and MCM-41 has shown the least catalytic activity in this acid catalytic reaction. The catalytic activity followed the order of  $\beta$ -Zeolite>Y-Zeolite >ZSM-5 >MCM-41.

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