



Research Article

An Efficient Knoevenagel Condensation using Phillipsite Zeolite as Catalyst in Liquid Phase Under Solvent Free ConditionsPriya Pawaiyaa^{1*}, Amrata Pawaiya², Nishi Agrawal¹ and Radha Tomar¹¹Ph.D student, School of Studies in Chemistry, Jiwaji University, Gwalior, M.P., India²Ph.D student, S. M. S. Govt. Model Science College, Gwalior M. P., India

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ABSTRACT

Ethyl-2-cyano3-phenyl acrylate (ECPA) used as an intermediate for the production of fine chemicals and pharmaceuticals was synthesized by Knoevenagel condensation of Benzaldehyde with ethyl cyanoacetate using Zn²⁺Phillipsite, Mg²⁺Phillipsite and H-Phillipsite Zeolite as a solid acid catalyst. Phillipsite was synthesized in the laboratory by hydrothermal method, after dealumination and calcination; the sample was characterized by different techniques such as powder X-ray diffraction analysis (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS) analysis. Effect of various reaction parameters such as reaction time, molar ratio of reactants, and weight of catalyst and reaction temperature were studied to optimize the reaction conditions. The optimum conditions for the synthesis of Ethyl-2-cyano3-phenyl acrylate (ECPA) were found at benzaldehyde to ethyl cyanoacetate molar ratio 1:1 using 0.1g of the catalyst at 140^oC. The product was analyzed by Gas Chromatography and the conversion of benzaldehyde to (ECPA) was found to be 67.9% in case of H-Phillipsite, 54.9 Zn²⁺Phillipsite and 59.7 Mg²⁺ Phillipsite Zeolite.

Keywords: Ethyl-2-cyano3-phenyl acrylate (ECPA); Knoevenagel condensation; Zn²⁺Phillipsite, Mg²⁺Phillipsite and H-Phillipsite Zeolite.

1. INTRODUCTION

The Knoevenagel condensation of aldehydes with active methylene compounds is an important and widely employed method for carbon-carbon bond formation inorganic synthesis¹⁻² with numerous applications in the synthesis of fine chemicals³, hetero Diels-Alder reactions⁴⁻⁵ and in synthesis of carbocyclic as well as heterocyclic⁶ compounds of biological significance. The reactions are usually catalyzed by bases⁷⁻⁹ such as amines, ammonia or sodium ethoxide in organic solvents. Lewis acids¹⁰ surfactants¹¹ zeolites¹² and heterogeneous catalysts¹³⁻¹⁴ have also been employed to catalyze the reactions. Similarly, the use of ionic liquids¹⁵⁻¹⁶ paves a new path for such organic synthesis. The use of environmentally benign solvents like water¹⁷⁻¹⁸ and solvent-free reactions represent very powerful green chemical technology procedures

from both the economical and synthetic point of view. They not only reduce the burden of organic solvent disposal, but also enhance the rate of many organic reactions. Therefore, efforts have been made to perform the Knoevenagel condensation in aqueous medium as well as in the absence of solvents¹⁹ which are usually catalyzed by Lewis acids²⁰, or base²¹⁻²² and require drastic conditions²³⁻²⁴. Some of these reactions are performed on solid supports, promoted by infrared²⁵, ultrasound or microwave²⁶⁻²⁷ heating.

Phillipsite is one of the rarer zeolites, but is popular among Zeolite collectors. It forms interesting aggregates that are commonly clustered into bright white spherules or balls with a rough crystalline or silky surface. Phillipsite is known to occur as an encrusting precipitate around hot springs. However, phillipsite is more commonly found in the vesicles or bubbles of volcanic rock as most other Zeolites. Zeolites are hydrated aluminosilicates of alkali metals and alkaline earths that can be

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visualized as hydrated equivalents of feldspar series. Although Zeolites have been recognized as a distinct mineral group since 1756 and have been employed as natural sieves in a variety of industrial uses for centuries, their potential importance as environmental indicators has only recently been perceived.

The present research work was aimed at providing a new insight into the emerging field of Zeolites and their conversion in to different catalytic forms for organic synthesis. Synthesis of different analogues of Zeolite such as Gobbinsite, Thomsonite and Phillipsite was carried out by hydrothermal method and were transformed in to Hydrogen, Zinc and Magnesium forms. Zeolites are stable, non-toxic and preventing contamination of valuable feedstock's. Zeolite is used as heterogeneous catalyst due to cavity, its thermal stability at higher temperature and selective even at unfavorable reactant ratio and the reaction is eco-friendly. For the research work three different Zeolites have been studied. The Zeolites viz. Gobbinsite, Thomsonite and Phillipsite are synthesized by hydrothermal synthesis. Catalyst plays an important role in organic reactions. Most of these catalysts are not recyclable and reusable. Some catalysts also tend to generate large quantities of wastes like wash metals that pose environmental threat. However, choosing a catalyst which is suitable for given reactions is often trial and error one approach is simple to try many catalysts as possible for the reactions.

2. MATERIALS AND METHODS

2.1. Chemicals

Sodium Silicate (Aldrich), Aluminium Nitrate, Sodium Hydroxide (Aldrich), Ammonium Nitrate (Merck), benzaldehyde with ethyl cyanoacetate were commercial samples from Merck.

2.2. Synthesis of the catalyst (Phillipsite)

Phillipsite is a tectosilicate mineral belonging to the Zeolite group. It is a hydrated sodium aluminium silicate of formula $(Ca, Na_2, K_2)_3 Al_6 Si_{10} O_{32} \cdot 12 H_2O$. Aluminium Nitrate as an aluminum source was mixed with an aqueous solution of NaOH. Then sodium silicate was added to the mixture and the mixture was homogenized by stirring. Finally, the gel was transferred to a Teflon-lined autoclave. The oven temperature was maintained

at 170°C for 24 hours. The product was recovered by filtration, washed thoroughly with deionized water and dried at 393 K overnight then calcined at 540°C for 5hrs. Phillipsite was then ion-exchanged with 1 M NH_4NO_3 three times. The material was then cooled to room temperature and kept in a desiccator prior to use. The catalyst was reactivated prior to use. Zn^{2+} ion-exchanged Phillipsite Zeolite (Zn^{2+} Phillipsite) was obtained by stirring H-Phillipsite with 0.1N Zinc nitrate solution (15 ml of solution per gram of catalyst) at 80°C (repeated three times), subsequent filtration and calcination in air at 550°C.

2.2. Catalyst characterization

The catalysts were characterized by XRD, SEM, FTIR and EDS analysis. The elements present in Zeolite were determined by energy dispersive X-ray (EDS) analysis using JEOL 5400 scanning microscope equipped with microprobe analyzer LINK ISIS (Oxford Instrument). Powder X-ray diffraction pattern for all the materials was recorded at room temperature on PW 1710 diffractometer. Samples were scanned using $Cu-K\alpha$ radiation of wavelength 1.54056 Å and the diffractograms were recorded in the range $2\theta = 0^\circ - 65^\circ$ at the scanning speed of 1 step / second. Powder diffraction pattern data is most commonly used as a "fingerprint" in the identification of a material. The morphology and crystal size of the synthesized material was examined by SEM. Samples were analyzed by using JSM-5600 microscope and the images obtained shows morphology of these materials. FT-IR spectroscopy was performed on SHIMADZU FT-IR spectrometer. The sample were prepared with KBr and pressed into wafer/pellet. Spectra were collected in the mid-IR region of 400 to 4000 cm^{-1} with a resolution of 1 cm^{-1} .

2.3. Catalytic activity studies

Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate was performed in a 25 ml round-bottom flask fitted with a reflux condenser. Nitrogen gas was purged into the flask in order to avoid oxidation of benzaldehyde and the purging of nitrogen was continued throughout the reaction. After attaining the requisite temperature, an appropriate amount of catalyst was added to the mixture. Aliquots of

reaction mixture were withdrawn at regular intervals and subjected to Gas Chromatographic analysis.

$$\% \text{ Conversion} = \frac{\text{Initial area} - \text{Final area}}{\text{Initial area}} \times 100$$

3. RESULTS AND DISCUSSION

3.1. Characterization

3.1.1. XRD

Powder X-ray diffraction pattern of Phillipsite Zeolite samples (sodium form and hydrogen form) are shown in Fig.1A, 1B and 1C. The peaks are characteristic of Zeolite compared to the diffraction pattern of standard Zn^{2+} Phillipsite, Mg^{2+} Phillipsite and H-Phillipsite Zeolite.

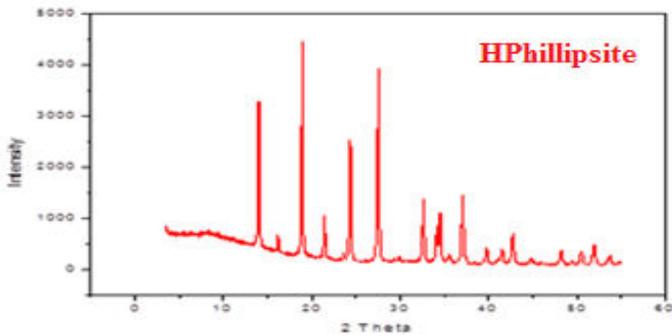


Fig. 1A XRD of Gobbinsite Zeolite

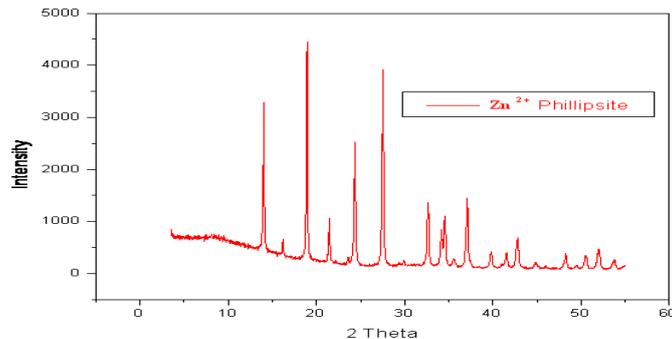


Fig. 1B XRD of Thomsonite Zeolite

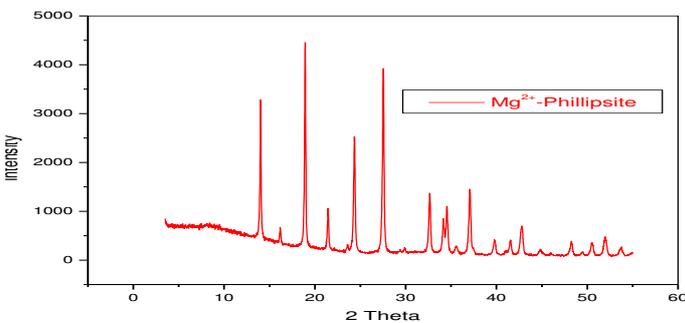


Fig.1C XRD of Phillipsite Zeolite

3.1.2. FTIR analysis

The FT-IR spectra (Fig.2A, 2B and 2C) shows the peaks between 700-850 cm^{-1} and 1000-1150 cm^{-1} are assigned to symmetric and antisymmetric T-O-T stretching vibration. The broad band in

the region of 3410 cm^{-1} is due to asymmetric stretching of OH group and the bands at 1621 and 1386 cm^{-1} due to bending vibration of (H-O-H) and - (O-H-O) - band respectively.

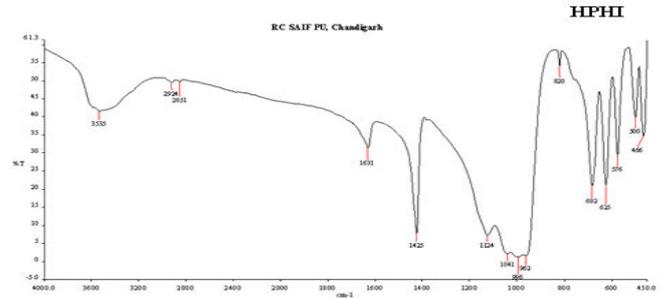


Fig.2A FTIR spectra of Phillipsite Zeolite

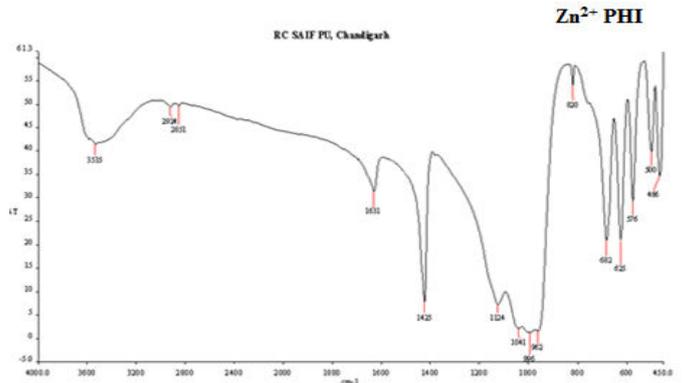


Fig.2B FTIR spectra of Phillipsite Zeolite

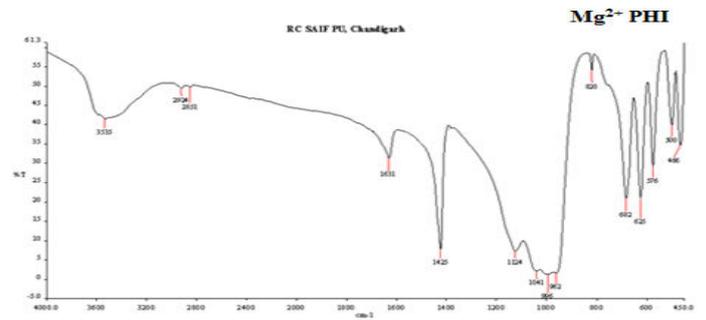


Fig.2C FTIR spectra of Phillipsite Zeolite

3.1.3. EDS analysis

The EDS spectra of samples presented in Fig.3A showed the presence of elements Si, Al and Na in the synthesized material.

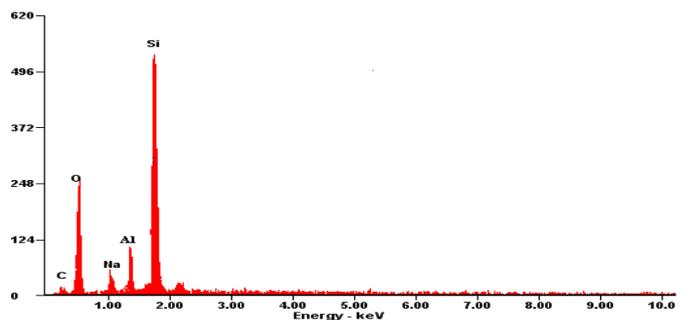


Fig.3A EDS Spectra of Phillipsite Zeolite

3.1.4. SEM analysis

Fig.4A represents the SEM micrograph of the synthesized material. The particle size of synthesized Phillipsite material was found to be 10 μ m.

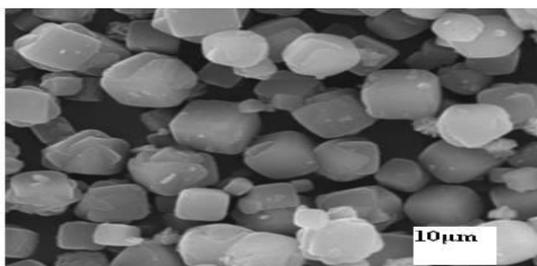


Fig. 4A SEM image of H- Phillipsite Zeolite

3.1.2. FTIR analysis

FTIR spectra of ethyl-2-cyano-3-phenyl acrylate (ECPA) shows band at 3032 cm^{-1} mainly due to the presence of C-H stretching of aromatic ring, C=O stretching occurs at 1729 cm^{-1} mainly due to carbonyl carbon, bands observed nearly at 900-1300 cm^{-1} due to C-O stretching of acrylate group.

In FTIR spectra of (ECPA) characteristic band observed at nearly 1729 cm^{-1} mainly due to C=O stretching vibration and 2225 cm^{-1} due to C \equiv N stretching vibration which is the characteristic vibration of acrylate.

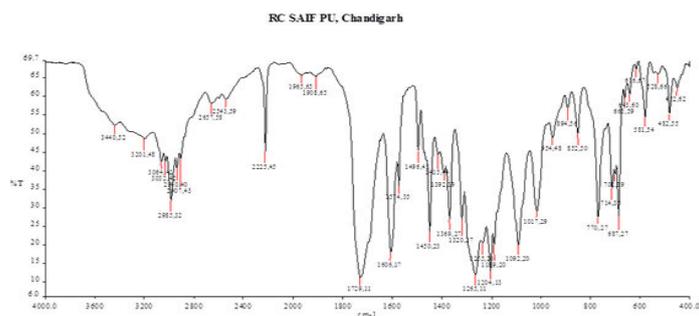


Fig. 5A FTIR spectra of ECPA (Ethyl-2-cyano3-phenylacrylate)

3.2. Catalytic activity

The catalytic activity of calcined Phillipsite was examined in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate. The gas chromatogram showed the presence of components, viz. benzaldehyde, ethyl cyanoacetate and ECPA over Phillipsite Catalysts.

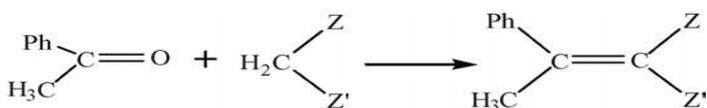


Fig.6A ECPA (Ethyl-2-cyano3-phenylacrylate)

3.2.1. Effect of reaction time

The Reaction was carried out at different reaction (refluxing) times. The reaction time was varied from 1 to 12 hrs. The conversion increased rapidly in the beginning and gradually leveled off after 4 hrs (Fig. 7A). For further studies the reaction time was fixed as 6 hrs.

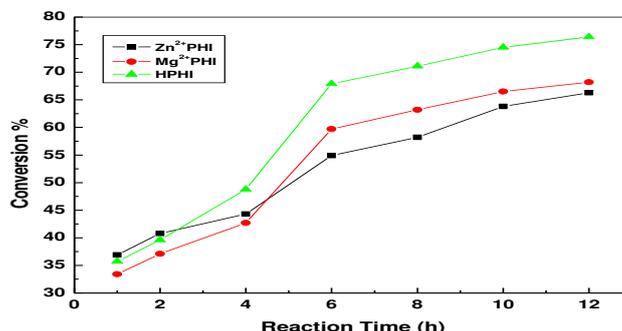


Fig.7A Effect of reaction time on conversion over ion exchanged analogues of PHI Zeolite

3.2.2. Effect of molar ratio of reactants

The effect of benzaldehyde to ethylcyanoacetate molar ratio was studied at 1:2, 1:1.5, 1:1, 1.5:1 and 2:1 by keeping the total volume constant (Fig.7B). The conversion of ECPA was found to increase with increase in concentration of benzaldehyde and ethylcyanoacetate and thereafter remained almost constant.

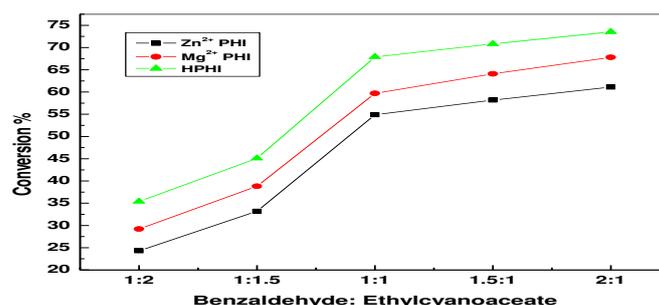


Fig.7B Effect of molar ratio of reactants on conversion over ion exchanged analogues of PHI Zeolite

3.2.3. Effect of amount of catalyst

The effect of catalyst quantity was studied over a range over of 0.25-1.5g for benzaldehyde to ECPA at 140 $^{\circ}$ C (Fig.7C). The conversion of ECPA was found to increase with increase in catalyst probably due to increase in the number of active sites and then the increase becomes less significant beyond 1g. This indicates that beyond 1g. The additional active sites do not increase the adsorption reactants and given concentration.

The influence of catalyst loading on the conversion of ECPA was carried out over H-Phillipsite and the results are presented in Fig 7C. As expected, the yield of ECPA increases with increase in the catalyst loading.

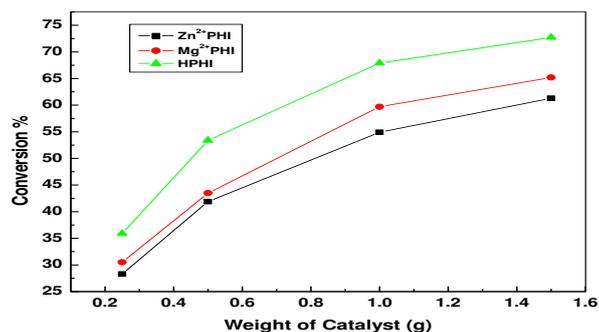


Fig.7C Effect of amount of Zeolite on conversion over ion exchanged analogues PHI Zeolite

3.2.4. Effect of reaction temperature

The effect of temperature was studied in order to establish the importance of activation energy in this reaction. The feed ratio was set at 1:1 and the reaction was studied over H-Phillipsite as this is more active than other catalysts. The results are presented in (Fig7D). The conversion of ECPA increases with increase in temperature, thus establishing the demand of high activation energy.

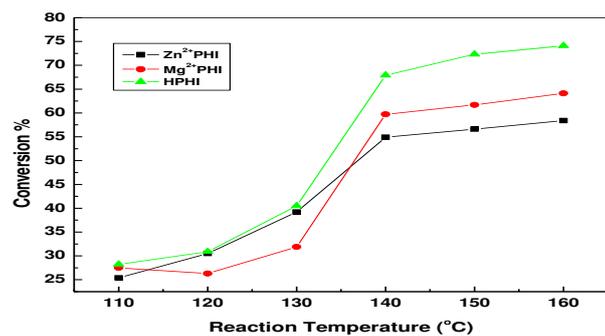
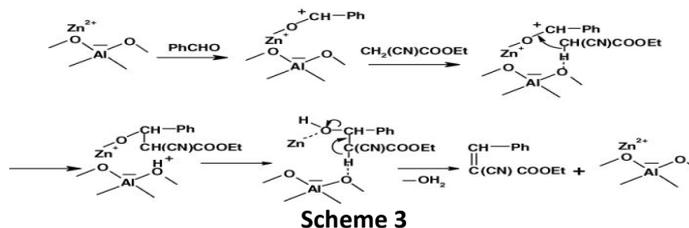
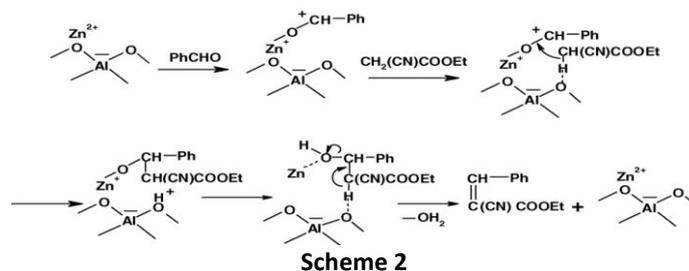
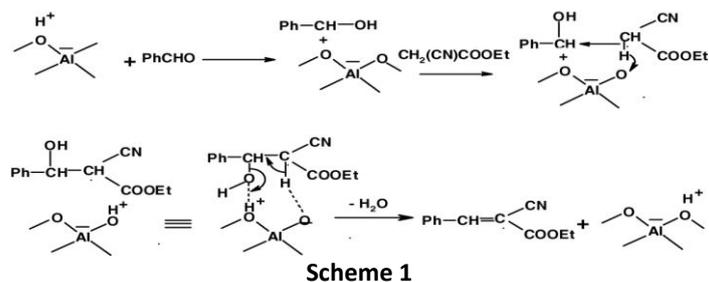


Fig.7D Effect of reaction temperature on conversion over ion exchanged analogues of PHI Zeolite



Proposed mechanism for Knoevenagel Condensation

4. CONCLUSION

The present work deals with synthesis of Zn²⁺Phillipsite, Mg²⁺Phillipsite and H-Phillipsite Zeolite was used as a solid acid catalyst for Knoevenagel condensation. The reaction parameters such as reaction time, temperature, benzaldehyde: ethyl cyanoacetate molar ratio and catalyst quantity were optimized. It was observed that after dealumination the pore size of Zeolite becomes larger and facilitates the reactant to enter into it and promoted the conversion of ethyl cyanoacetate to ECPA (Ethyl-2-cyano-3-phenylacrylate). Under the optimum reaction conditions (temperature 140°C, benzaldehyde: ethyl cyanoacetate mole ratio of 1:1, and reaction time for 6 hrs) conversion of ethyl cyanoacetate to ECPA (Ethyl-2-cyano-3-phenylacrylate) was found to be 67.9% in case H-Phillipsite 54.9% Zn²⁺ Phillipsite and 59.7% Mg²⁺ Phillipsite Zeolite.

5. ACKNOWLEDGEMENTS

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