

Synthesis, Characterization of Thomsonite Zeolite for Knoevenagel Condensation

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Abstract

Ethyl-2-cyano-3-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⁺Thomsonite, Mg²⁺Thomsonite and H-Thomsonite Zeolite as a solid acid catalyst. Thomsonite was synthesized in the laboratory by hydrothermal method, after dealumination and calcinations; 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 condition for the synthesis of Ethyl-2-cyano-3-phenyl acrylate (ECPA) was found at benzaldehyde with ethyl cyanoacetate molar ratio 1:1 using 0.1g of the catalyst at 1400C. The product was analyzed by Gas Chromatography and. The conversion of benzaldehyde to (ECPA) was found to be 50.7% in case of H-Thomsonite, 40.8% Zn²⁺Thomsonite and 45.6% Mg²⁺Thomsonite.

Keywords: Ethyl-2-cyano-3-phenyl acrylate (ECPA); Knoevenagel condensation; Zn²⁺Thomsonite, Mg²⁺Thomsonite and H- Thomsonite Zeolite.

Introduction

The Knoevenagel condensation of aldehydes with active methylene compounds is an important and widely employed method for carbon-carbon bond formation in organic synthesis [1-2] with numerous applications in the synthesis of fine chemicals, [3] hetero Diels-Alder reactions [4-5] and in synthesis of carbocyclic as well as heterocyclic [6] compounds of biological significance. The reactions are usually catalyzed by bases [7-9] such as amines, ammonia or sodium ethoxide in organic solvents. Lewis acids, [10] surfactants, [11] zeolites [12] and heterogeneous catalysts [13-14] have also been employed to catalyst the reactions. Similarly, the use of ionic liquids [15-16] paves a new path for such organic synthesis. The use of environmentally benign solvents like water [17-18] 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 solvents [19] which are usually catalyzed by Lewis acids, or



base and require drastic conditions. Some of these reactions are performed on solid supports, promoted by infrared, ultrasound or microwave heating.

Thomsonite is the name of series of tecto-silicate minerals of the Zeolite group. Prior to 1997, Thomsonite was recognized as a mineral species, but a reclassification in 1997 by International Mineralogical Association changed it to a series name, with the mineral species being named Thomsonite-Ca and Thomsonite-Sr. Strontium can substitute for calcium and the name of species depends on the dominant element. The species are visually indistinguishable and the series name Thomsonite is used whenever testing has not been performed. Globally, Thomsonite is one of the rarer Zeolite. It forms tight acicular radiating clusters and spherules as well as some blockier crystals that are found in the vesicles or bubbles of volcanic rock as are most other zeolites. Natrolite, another Zeolite, is usually square in cross section but is otherwise difficult to distinguish from Thomsonite. The color is usually colorless or white, but a few specimens have shown a lovely yellow color. Thomsonite is a rare mineral and is sought after by collectors of rare Zeolite minerals.

Zeolites are hydrated aluminosilicates of the alkali metals and alkaline earths that can be visualized as hydrated equivalents of the 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.

Acidification of Earth's terrestrial and oceanic biospheres is now receiving growing attention. This acidification is due to two anthropogenic sources. The first is land acidification, which is caused by nitric and sulfuric acid. The second is ocean acidification, which is due to storage of CO₂ released by human. As a response to the problem of acidification, scientists have to develop their knowledge about the acid-base properties of natural minerals. One of the most important natural minerals is zeolites group, which has a continuous conjugated network of SiO₄ and AlO₄ tetrahedral. Adjacent tetrahedral are linked at their corners via a common oxygen atom, which result in an inorganic macromolecule with structurally distinct three-dimensional framework. Zeolites acidity arises from the substitution of Si⁴⁺ by Al³⁺. This substitution creates a negative charge that requires a proton (or another positive ion: Na⁺, K⁺, Mg²⁺, Ca²⁺, etc.) to be balanced. The acid-base properties of zeolites are also very important in determining their catalytic activity and their adsorption behavior toward pollutants. The satisfactory application of surface complexation models to describe the adsorption of metal ions onto clays and minerals is limited by the availability of information about the surface acid sites density of these materials. The acidity of synthetic zeolites has been extensively studied because of its importance in catalysis applications. Numerous techniques have been devoted to the investigation of the nature, strength, and distribution of the acid sites in synthetic zeolites.

Experimental

Chemicals

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

Synthesis of the catalyst (Thomsonite)

Thomsonite is a tectosilicate mineral species belonging to the Zeolite group. It is a hydrated sodium and aluminium silicate with the formula $(\text{NaCa}_2)\text{Al}_5\text{Si}_5\text{O}_{20}\cdot 6\text{H}_2\text{O}$, Hydrated Calcium Sodium. Aluminium Nitrate as the 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 5 h. The Thomsonite was then ion-exchanged three times with 1 M NH_4NO_3 . The material was then cooled to room temperature and kept in a desiccator prior to use. The catalyst was preactivated prior to use. Zn^{2+} ion-exchanged Thomsonite Zeolite (Zn^{2+} Thomsonite) was obtained by stirring H-Thomsonite 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 .

Catalyst characterization

The catalysts were characterized by XRD, SEM, FTIR and EDS analysis. The elements present in the Zeolite were determined by energy dispersive X-ray (EDS) analysis using JEOL 5400 scanning microscope equipped with the microprobe analyzer LINK ISIS (Oxford Instrument). Powder X-ray diffraction pattern for all the materials were recorded at room temperature on PW 1710 diffractometer. Samples were scanned using Cu- α radiation of wavelength 1.54056 \AA 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. If possible, the diffraction experiment should be adopted to optimize that feature which provides the desired information. 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 the 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 range of 400 to 4000 cm^{-1} with a resolution of 1 cm^{-1} .

Catalytic activity studies

Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate was performed in a 25 ml round-bottomed 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 the reaction mixture were withdrawn at regular intervals and subjected to Gas Chromatographic analysis (Shimadzu GC-17 A; cross-linked 5% phenylmethylsiloxane capillary column (DB-5, 30 m), FID detector). The products were also identified by GC-MS using a Perkin-Elmer Auto System XL Gas Chromatograph with Turbo Mass Spectrometer (EI, 70 eV) using helium as carrier gas.

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

Results and discussion

Characterization

XRD

Powder X-ray diffraction pattern of synthesized materials was recorded at room temperature on PW 1710 diffractometer. Samples were scanned using Cu-K α 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. The XRD pattern of Thomsonite Zeolite samples (sodium form and hydrogen form) are shown in Fig. 1. The peaks are characteristic of Zeolite which was compared to the diffraction pattern of Zn²⁺Thomsonite, Mg²⁺Thomsonite and H-Thomsonite Zeolite.

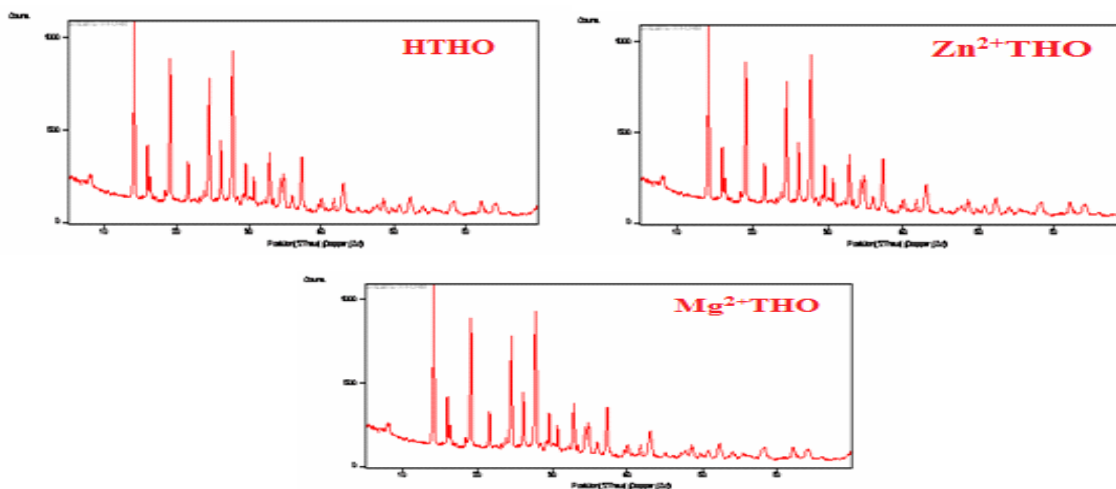


Fig.1 XRD of Thomsonite Zeolite

FTIR analysis

FT-IR spectroscopy was performed on SHIMADZU FT-IR spectrometer. The samples were prepared with KBr and pressed into wafer/pellet. Spectra were collected in the mid-IR range of 400 to 4000 cm⁻¹ with a resolution of 1cm⁻¹. Fig.2 shows the peaks between 700-850 cm⁻¹ and 1000-1150 cm⁻¹ are assigned to symmetric and antisymmetric T-O-T stretching vibration, broad band in the region of 3410 cm⁻¹ due to asymmetric stretching of OH group and the bands at 1621 and 1386 cm⁻¹ due to bending vibration of (H-OH) and -(O-H-O)- band respectively.

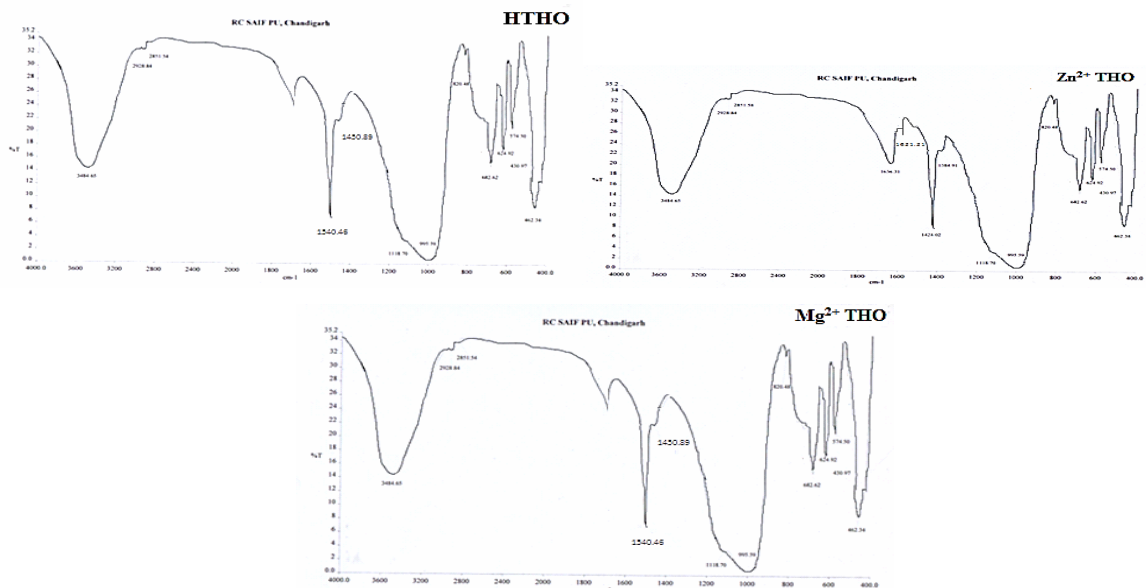


Figure 2 FTIR spectra of Thomsonite Zeolite

EDS analysis

The EDS spectra of the samples are presented in Fig.3 were measured on a JEOL 5400 scanning microscope equipped with the microprobe analyzer LINK ISIS (Oxford Instrument) for the analysis of the element. EDS analysis showed the presence of Si, Al and Na in the synthesized material.

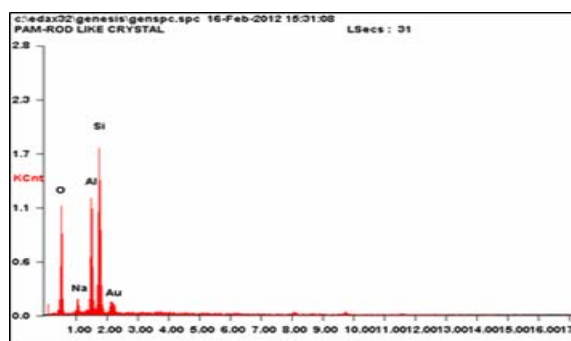


Figure 3 EDS spectra of H- Thomsonite zeolite

SEM analysis

For SEM analysis samples were analyzed by using JSM-5600 microscope, Fig.4 represents the SEM micrograph of the synthesized material. The particle size of the synthesized material was found to be 5 micrometer.

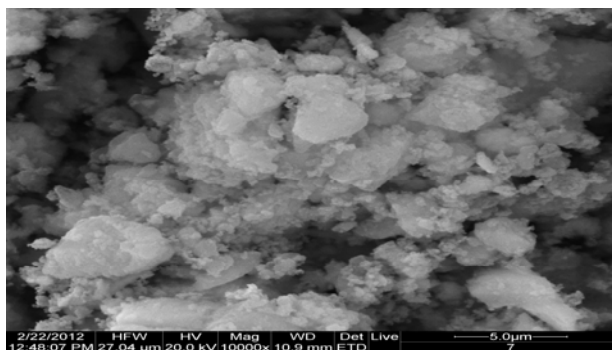
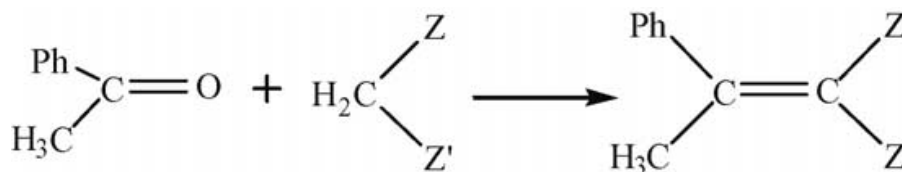


Figure 4 SEM image of H- Thomsonite Zeolite

Catalytic activity

The catalytic activity of the calcined Thomsonite was examined in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate. The GC showed the presence of only four components, i.e., benzaldehyde, ethyl cyanoacetate and ECPA over Thomsonite Catalysts.



Effect of reaction time

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. 5). For further study the reaction time was fixed as 6 hrs.

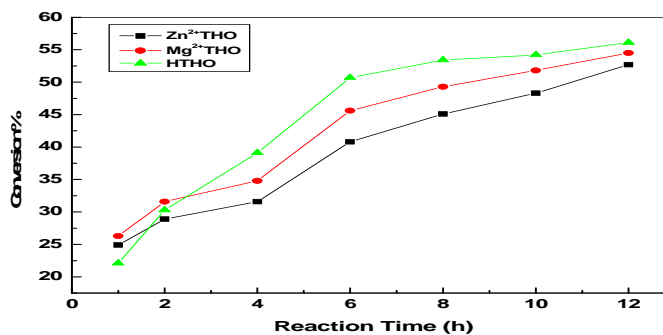


Figure 5 Effect of reaction time on conversion over ion exchanged analogues of Thomsonite Zeolite

Effect of molar ratio of the 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.6). The conversion of ECPA was found to increase with increase in concentration of benzaldehyde and ethyl cyanoacetate and thereafter remained almost constant.

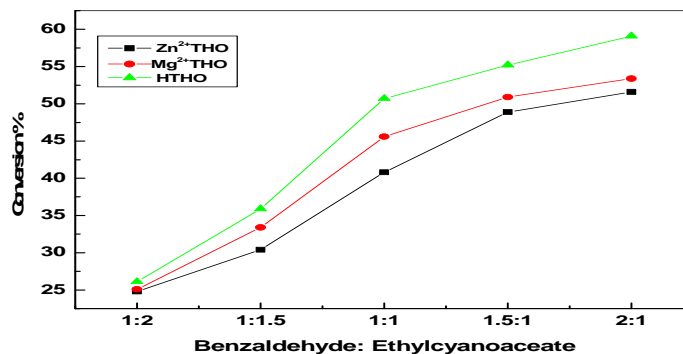


Figure 6 Effect of amount of Zeolite on conversion over ion exchanged analogues Thomsonite Zeolite

Effect of amount of catalyst

The effect of catalyst quantity was studied over a range over of 0.25-0.15g for benzaldehyde to ECPA at 1400C (Fig.7). The conversion of ECPA was found to increase with increase in catalyst amount which is due to the proportional increase in the number of active sites and then increase becomes less significant beyond 0.1g. This indicates that beyond 0.1g. 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-Thomsonite and the results are presented in Fig 7. As expected, the yield of ECPA increases with increase in the catalyst loading.

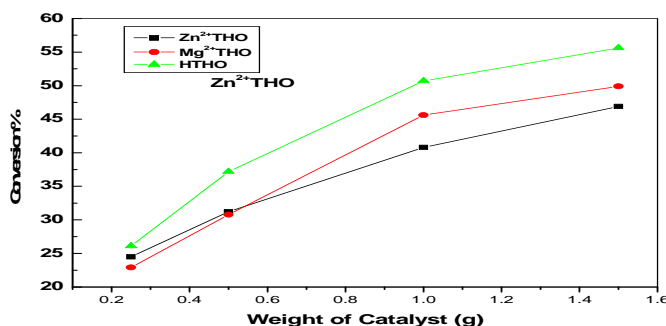


Figure 7 Effect of molar ratio of reactants on conversion over ion exchanged analogues of Thomsonite Zeolite

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-Thomsonite as this is more active than other catalysts. The results are presented in (Fig 8). The yield of ECPA increases with increase in temperature, thus establishing the demand of high activation energy.

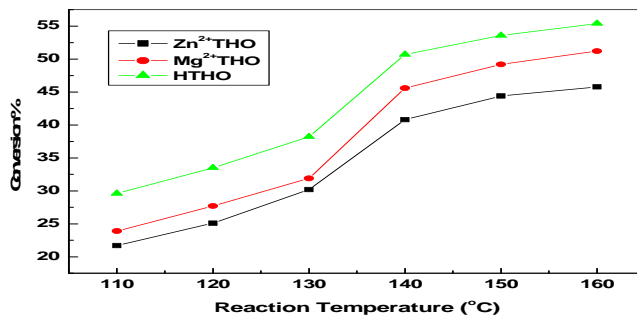
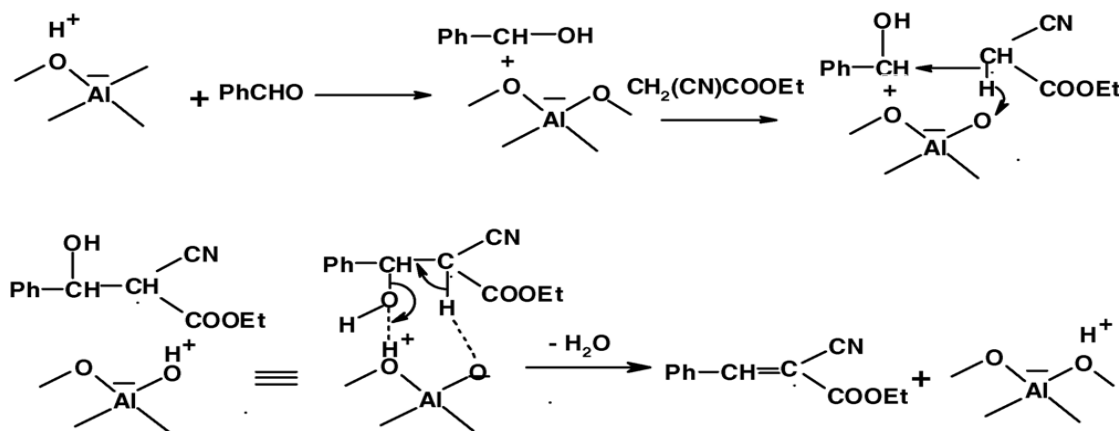
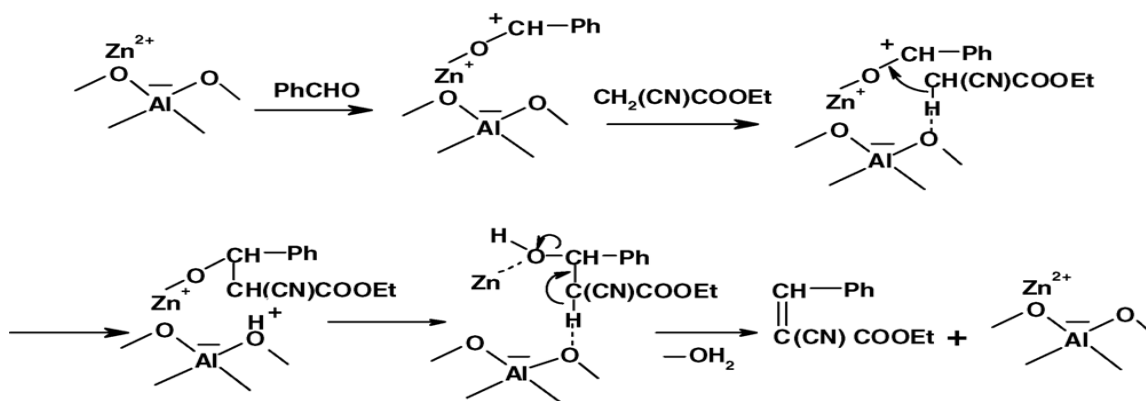


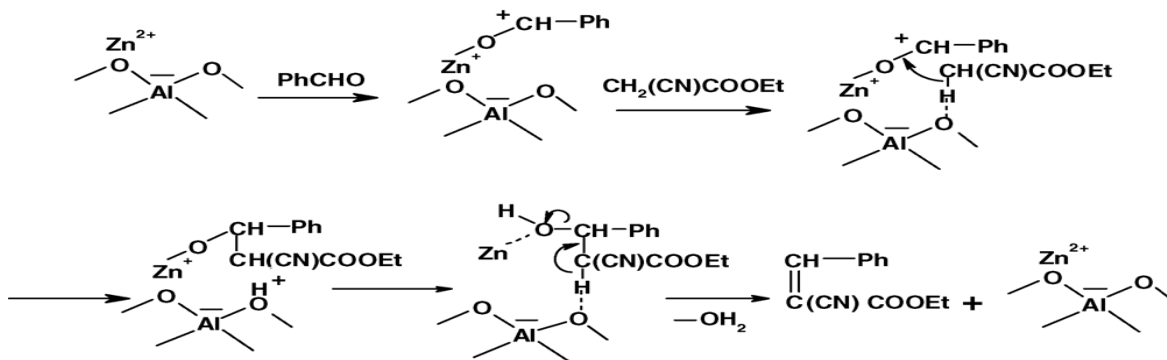
Fig.8 Effect of reaction temperature on conversion over ion exchanged analogues of Thomsonite Zeolite



Scheme 1.



Scheme 2.



Scheme 3.

Proposed mechanism for the Knoevenagel Condensation

Conclusion

The present work deals with the synthesis of Zn^{2+} Thomsonite, Mg^{2+} Thomsonite and H-Thomsonite Zeolite, use as a solid acid catalyst for Knoevenagel condensation. The reaction parameters such as reaction time, temperature, and benzaldehyde: ethyl cyanoacetate molar ratio and catalyst quantity were optimized. It was observed that after dealumination the pore size of Zeolite becomes larger and facilitate the reactant to get entered into it and promoted the conversion of ethyl cyanoacetate to ECPA. Under the optimum reaction conditions (140°C, benzaldehyde: ethyl cyanoacetate mole ratio of 1:1, and reaction time for 6 hrs) conversion of ethyl cyanoacetate to ECPA was found 67.9% in case H-Thomsonite Zeolite respectively.

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