



## **SYNTHESIS AND CHARACTERIZATION OF ANALOGUE OF HEULANDITE ZEOLITE USED AS CATALYSTS IN CANNIZZARO REACTION**

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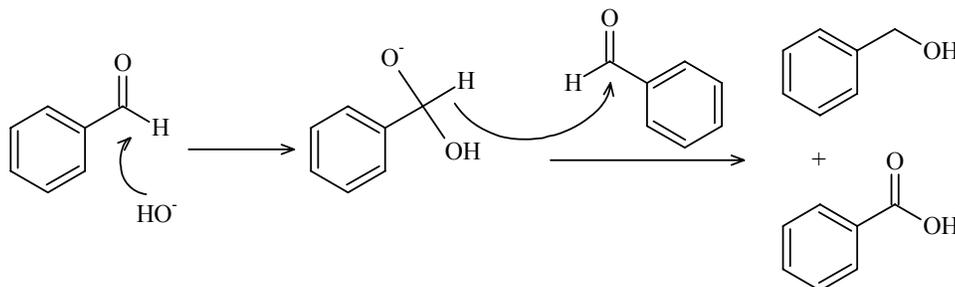
### **ABSTRACT**

Heulandite was synthesized in the laboratory by hydrothermal method using sodium tri-silicate and aluminum nitrate as silica and alumina source. The calcinations of synthesized material were carried out at 540°C and sample was characterized by different techniques such as powder X-ray diffraction analysis (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). p-nitrobenzaldehyde used as an intermediate for the production of fine chemicals and pharmaceuticals was synthesized by Cannizzaro reaction by refluxing in DMF solvent, where p-nitrobenzaldehyde was converted to p-nitrobenzyl alcohol and p-nitro benzoic acid by self-oxidation-and-reduction. 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 p-nitrobenzaldehyde was found at p-nitro benzoic acid, p-nitro benzyl alcohol molar ratio 8 : 1, using 0.040 g of the catalyst at 80°C. The product was analyzed by Gas Chromatography with FID detector. The conversion of p-nitrobenzaldehyde to p-nitrobenzoic acid and p-nitrobenzyl alcohol was found to be 29.6% (p-NBA) and 8.3% (p-NBOH) form of H-Heulandite Zeolite respectively.

**Key words:** Oxidation, p-nitrobenzaldehyde, H-Heulandite, Cannizzaro reaction.

### **INTRODUCTION**

The Cannizzaro reaction, named after its discoverer Stanislao Cannizzaro, is a chemical reaction that involves the base-induced disproportionation of an aldehyde lacking a hydrogen atom in the alpha position<sup>1,2</sup>. Cannizzaro first accomplished this transformation in 1853, when the obtained benzyl alcohol and benzoic acid from the treatment of benzaldehyde with potash (potassium carbonate).



Zeolites have homogeneous crystalline structures, and hence shape-selective reactions using them

were achieved and reported. Zeolite is crystalline hydrated aluminosilicates of the alkaline earths. Natural zeolites are formed in several geological environments such as hydrothermal, burial metamorphic, closed system (including alkaline earths), open system, and weathering profiles. Due to their remarkable physical and chemical properties, zeolites have been utilized successfully by the chemical industry and in environmental protection over the last 40 years<sup>3</sup>. We have been interested in the application of zeolite to organic reactions in the liquid phase and have reported that zeolite performed the shape-selective hydrolysis of esters<sup>4</sup> and ring-opening reaction of peroxides<sup>5</sup>. Generally, aromatic aldehydes and aliphatic ones with no  $\alpha$ -hydrogen, give the Cannizzaro reaction when treated with NaOH or other strong bases. In place of these liquid bases, a clean chemical procedure using environmentally friendly solid base such as zeolite is desirable. The application of solid acid as a catalyst makes separation process easy in the reaction. This paper reports that zeolites, especially H-Heulandite type effectively catalyzed the reaction in liquid phase. The use of zeolites as catalyst for organic reactions began in early 1960s. Due to these properties zeolites have been found to be a safe alternative for such conventional liquid acid catalysts used in synthetic organic chemistry in petroleum refining, fine chemical synthesis and pharmaceutical industries, etc.<sup>6-8</sup>

Natural zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations and consist of infinitely extending three dimensional network of  $\text{AlO}_4^{5-}$  and  $\text{SiO}_4^{4-}$  tetrahedral, linked by sharing of all oxygen atoms. Certain zeolite frameworks are ordered, porous crystalline having a definite structure and voids, which may be interconnected by number of channels. The internal structure of these frameworks is hydrophilic. Owing to a large internal surface area and considerable costs than synthetic counterparts such as Heulandite specimens have attracted researches working in the area of catalysis<sup>9-12</sup>.

Zeolite mineral species shall not be distinguished solely on the basis of the framework Si/Al ratio<sup>13</sup>. Individual species in a zeolite mineral series with varying extra framework cations are named by attaching to the series name a suffix indicating the chemical symbol for the extraframework element that is most abundant in atomic properties, e.g. Heulandite-Ca, Heulandite-Na, Clinoptilolite-K, Clinoptilolite-Ca etc.<sup>14</sup>

A potential catalytic application of a pure heulandite is the isomerization of but-1-ene to 2-methylpropene as suggested by the recent work of Woo et al.<sup>15</sup> To date, synthesis of heulandite type zeolites has proven exceedingly difficult. There are two reported synthetic routes to Heulandite. One of these requires extreme conditions of pressure and temperature ( $P > 1000 \text{ atm}$ ,  $T > 250^\circ\text{C}$ ) and the other involves synthesis times of 40 to 80 d. Additionally, several preparations of Clinoptilolite are also given in the literature.<sup>16-21</sup>

For industrial purposes, homogeneous catalysts have shown some disadvantages, which among others are high consumption of catalysts and problem in the separation step due to similar phases of the reaction products to that of the catalyst. In addition, the use of acidic reagents in aqueous form also creates environmental problems such as corrosion.

Heterogeneous catalyst has been given much attention to overcome the problems. Solid catalysts such as zeolites<sup>22-33</sup>, phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) supported on  $\text{SiO}_2$  in the form of cerium salt<sup>34</sup>, mesoporous molecular sieves such as MCM-41<sup>35</sup> and clay such as montmorillonite<sup>36</sup> are among the solid acid catalysts that have been used in Cannizzaro reaction.

## EXPERIMENTAL

### Chemicals

Sodium silicate (Aldrich), Aluminium nitrate, Sodium hydroxide (Aldrich), Ammonium nitrate (Merck), p-Nitrobenzaldehyde (Himedia), DMF (N, N Dimethyl Formamide) were commercial samples from Merck.

## Synthesis of the catalyst (Heulandite)

Heulandite is a tectosilicateminerals species belonging to the zeolite group. It is a hydrated sodium and aluminiumsilicate with the formula  $(Ca, Na)_{2-3}Al_3 (Al, Si)_2 Si_{13}O_{36}.12H_2O$ , Hydrated calcium sodium aluminum silicate. 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 hrs. The Heulandite was then ion-exchanged three times with 1 M  $NH_4NO_3$ .

## Catalyst characterization

The catalysts were characterized by XRD and FTIR 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 analyser 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-K  $\alpha$  radiation of wavelength 1.54056 Å and the diffractograms were recorded in the range  $2\theta = 0^\circ - 28^\circ$  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. FTIR spectroscopy was performed on Shimadzu FTIR 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

The liquid phase p-nitrobenzaldehyde and N,N dimethyl bezaldehyde (solvent) was carried out in a 100 mL round bottom flask fitted with water cooled condenser in the temperature rang 80°C under atmospheric pressure. The temperature was maintained by using an oil bath connected to thermostat. Both the reactants were taken directly into the RB flask along with the catalyst. The reaction mixture was continuously stirred during the reaction using a magnetic stirrer and then the clear solution of the reaction mixture was withdrawn periodically and was analyzed by Gas Chromatograph (Varian vista 6000) fitted with a (AT-Wax column diameter 0.25 mm, thickness 0.2 mm and length 30 m) FID detector and qualitatively by GC (Shimadzu). The conversion was expressed by the percentage of p-nitrobenzaldehyde converted into the p-nitrobenzoic acid and p-nitrobenzyl alcohol product. Experiment was designed by varying amount of catalyst, molar ratio of the reactants and reaction temperature and reaction period to obtain optimum reaction condition.

The conversion % of organic compound was obtained by the following formula.

$$\text{Conversion \%} = \{ \text{Initial area} - \text{final area} / \text{Initial area} \} \times 100$$

## Reaction procedure

A typical example of Cannizzaro reaction of p-nitrobenzaldehyde is illustrative; zeolite heulandite (0.040 g) and its H-form are used as catalyst in this reaction. p-nitrobenzaldehyde (0.378 g) was added in 10 mL of (DMF solvent) in flask and the suspension was refluxed with magnetic stirrer for 40 h at 80°C temperature. Aliquot of reaction mixture was analyzed by gas chromatography (GC).

## Solvent used

N, N-Dimethyl formamide (DMF) was added the most effective solvent in reaction medium. Its

appearance is a clear liquid soluble in water. It is organic compound, common compound and polar in nature (Aprotic solvent) with high boiling point. The reaction follows the polar mechanism such as  $S_N2$  mechanism.

## 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 $\alpha$  radiation of wavelength 1.54056 Å and the diffractograms were recorded in the range  $2\theta = 0^\circ - 28^\circ$  at the scanning speed of 1 step / second. The XRD pattern of Heulandite zeolite samples (Sodium form and Hydrogen form) are shown in Fig. 1 and 2. The peaks are characteristic of Heulandite zeolite, which was compared to the diffraction pattern of Heulandite zeolite.

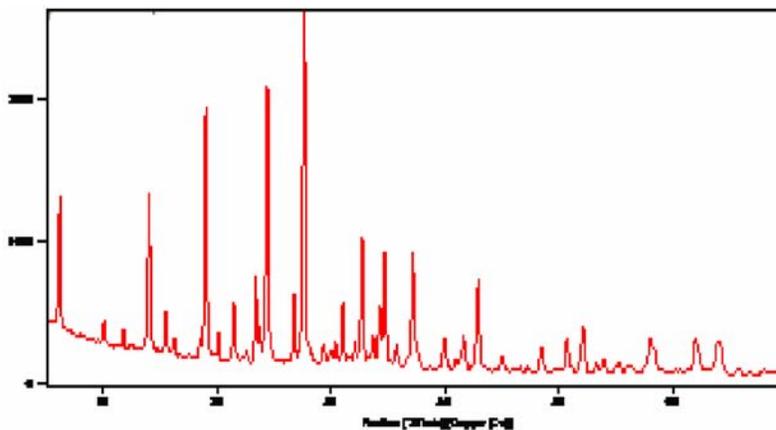


Fig. 1: XRD of Heulandite zeolite

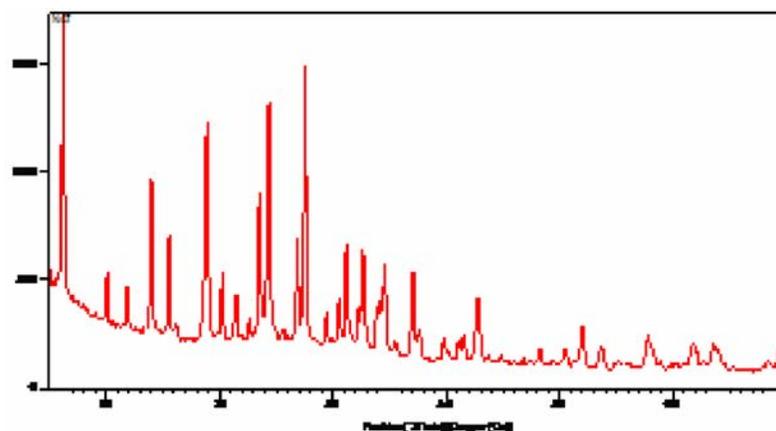


Fig. 2: XRD of H-Heulandite zeolite

#### FT-IR 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  $4000\text{ cm}^{-1}$  with a resolution of  $1\text{ cm}^{-1}$ .

Figs. 3 and 4 show the peaks between  $682\text{--}820\text{ cm}^{-1}$  and  $995\text{--}1118\text{ cm}^{-1}$  are assigned to symmetric and antisymmetric T-O-T stretching vibration, broad band in the region of  $3484\text{ cm}^{-1}$  due to asymmetric stretching of OH group and the bands at  $1636$  and  $1384\text{ cm}^{-1}$  due to bending vibration of (H-OH) and (O-H-O) band, respectively.

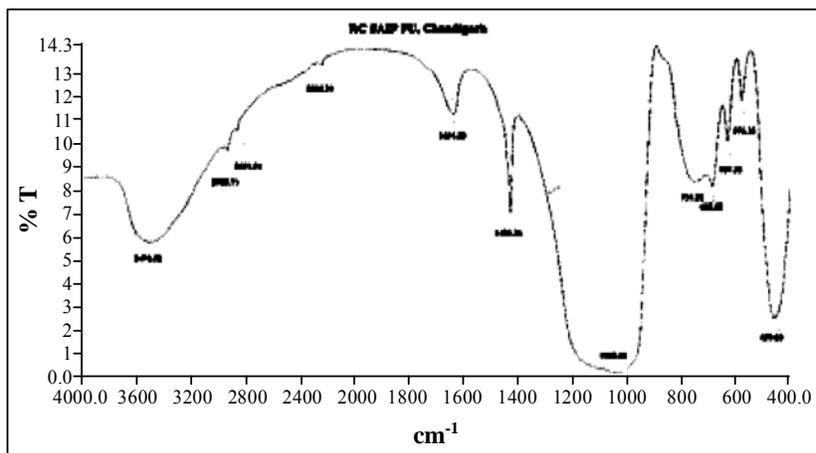


Fig. 3: FT-IR spectra of heulanite zeolite

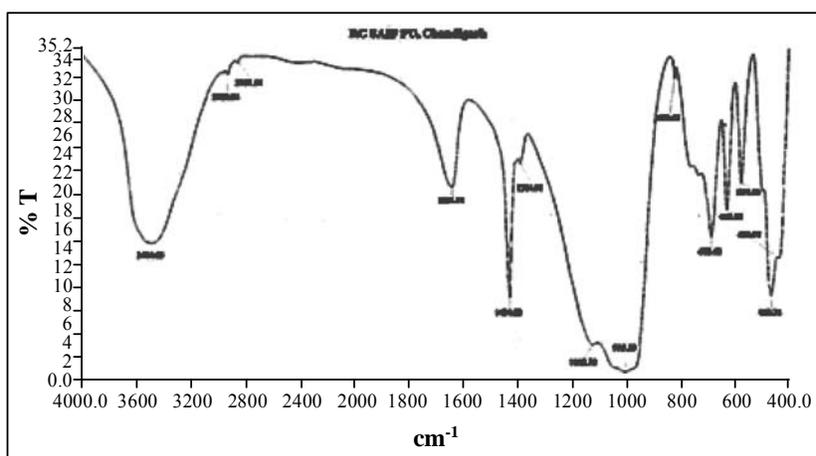


Fig. 4: FT-IR spectra of H-Heulanite zeolite

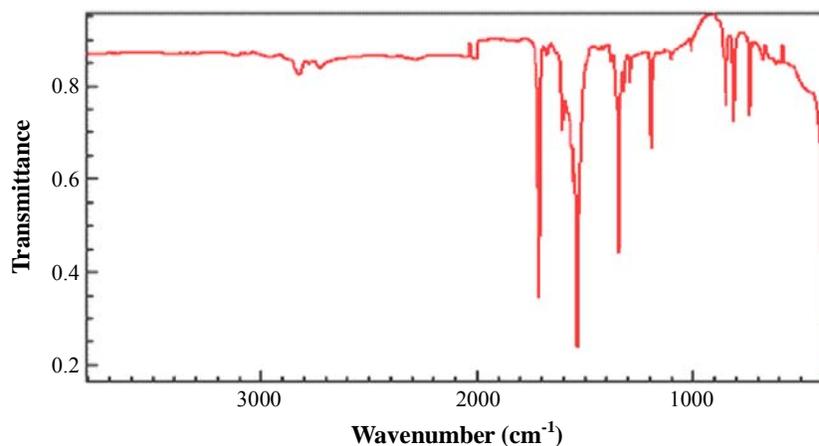
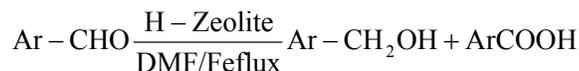


Fig. 5: FT-IR spectra of p-nitrobenzaldehyde

### Catalytic activity

The catalytic activity of the calcined Heulandite was examined in the Cannizzaro reaction oxidation of p-nitrobenzoic acid and p-nitrobenzyl alcohol. The GC and GC-MS analysis showed the presence of only four components, i.e., N, N dimethyl formamide, p-nitrobenzaldehyde and p-nitrobenzoic acid and p-nitrobenzyl alcohol over H-Heulandite and dealuminated H-Heulandite catalysts.



### Effect of reaction time

The effect of crystallization time on the morphology of Heulandite zeolite was studied in series by the synthesis performed with reference to composition of some Heulandite zeolite material in the crystallization time 10-40 hours. The increase in time and formation of larger crystals with more uniformity in practical size in comparison to crystals of material, synthesized at 80°C temperature. The evolution of the characteristic data suggest than in the 10-40 hours synthesis period crystalline nature of material is observed but beyond this crystalline phase comes in to existence. Heulandite zeolite. Fig. 6. shows the Heulandite maximum conversion 40 hrs at 29.6% of p-nitrobenzoic acid and 8.3% of p-nitrobenzyl alcohol.

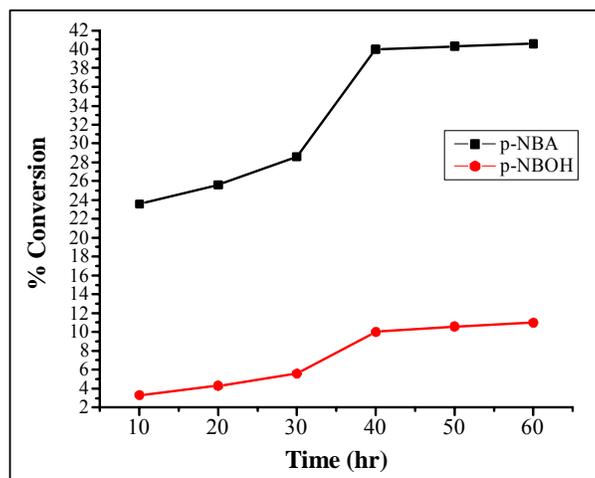


Fig. 6: Effect of reaction time on conversion over Heulandite

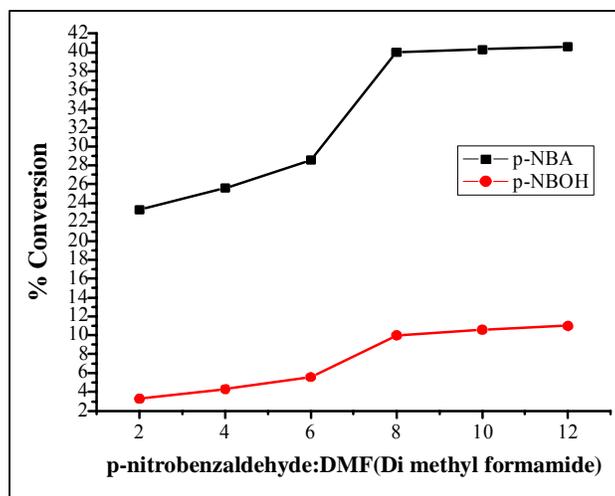
### Effect of molar ratio of the reactants

The effect of p-nitrobenzaldehyde to p-NBA and p-NBOH molar ratio was studied at 2 : 1, 4 : 1, 6 : 1, 8 : 1 and 10 : 1 by keeping the total volume constant (Fig. 7). The conversion of p-nitro benzoic acid and p-nitro benzyl alcohol was found to increase with increase in concentration of p-nitrobenzaldehyde up to eight and thereafter remained almost constant. The increasing conversion of p-nitrobenzoic acid and p-nitrobenzyl alcohol. Further increase in molar ratio has no appreciable effect in p-nitrobenzaldehyde and p-nitro benzyl alcohol conversion.

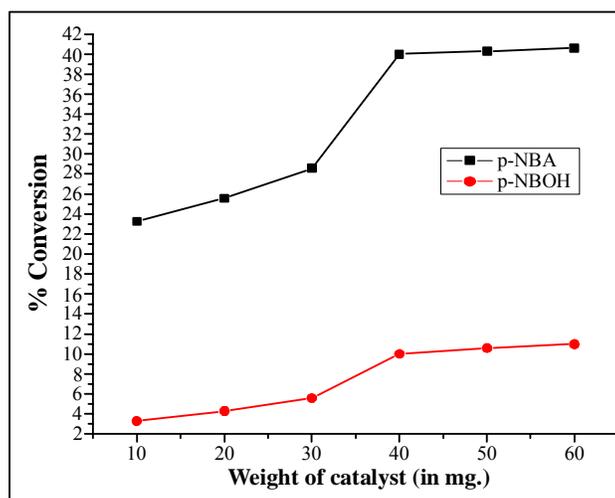
### Effect of amount of catalyst

The effect of catalyst quantity was studied over a range over of 0.010-0.060 g for benzaldehyde to p-NBA and p-NBOH at 80°C. The conversion of p-NBA or p-NBOH 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 0.040 g. This indicates that beyond 0.040 g. The additional active sites do not increase the adsorption reactants and given concentration (Fig. 8).



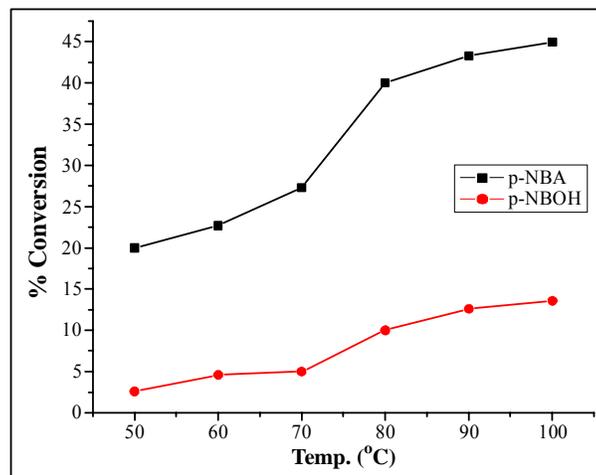
**Fig. 7: Effect of molar ratio of reactants on conversion of p-nitrobenzaldehyde**



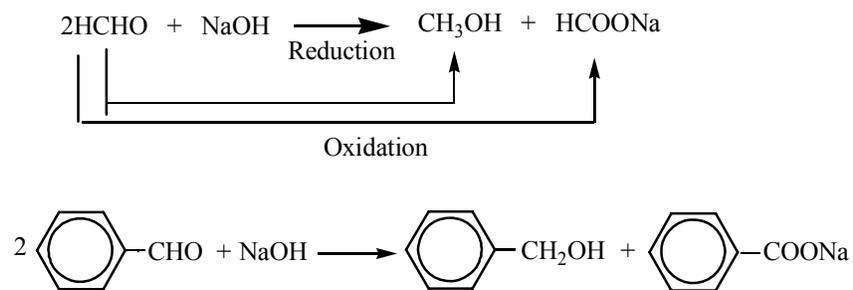
**Fig. 8: Effect of catalyst loading on conversion of p-nitrobenzaldehyde**

### Effect of reaction temperature

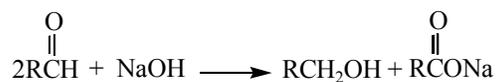
The effect of reaction temperature on the conversion of p-nitrobenzaldehyde was studied over a range of 50-100°C (Fig. 9). The conversion was found to increase significantly with increase in temperature till 80°C and thereafter a slight decrease was observed. Fig. 9 shows the effect of the reaction temperature on the conversion of p-nitrobenzaldehyde into p-nitrobenzoic acid and p-nitrobenzyl alcohol over Heulandite zeolite, respectively. The conversion of p-nitrobenzaldehyde increased with the reaction temperature over these zeolites. The equilibration temperature was calculated by these data where the conversion distance of p-nitrobenzaldehyde into p-nitrobenzoic and alcohol was found minimum in reaction period. Reaction temperature was increased 50-100°C where we found equilibration temperature 80°C.



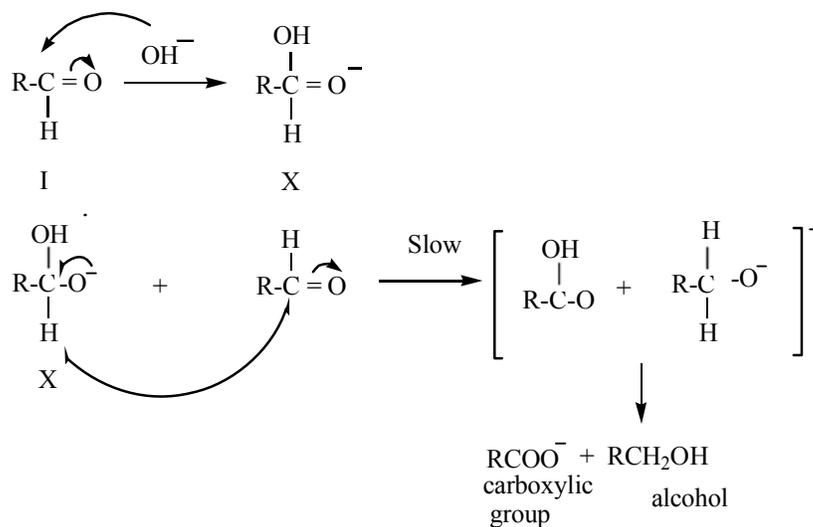
**Fig. 9: Effect of reaction temperature on conversion over Heulandite**



### Mechanism



### Step-I



**Mechanism of Cannizzaro reaction involves a hydride shift<sup>33</sup>**

## CONCLUSION

The present work deals with the synthesis of zeolites Heulandite, and use as a solid acid catalyst for self-oxidation and reduction of p-nitrobenzoic acid and p-nitrobenzyl alcohol. The reaction parameters such as reaction time, temperature, and oxidation: p-nitrobenzaldehyde molar ratio and catalyst quantity were optimized. Under the optimum reaction conditions (p-nitrobenzaldehyde : p-NBA and p-NBOH mole ratio of 8 : 1, and reaction time for 40 hrs) conversion of p-nitrobenzaldehyde to p-nitrobenzoic acid and p-nitrobenzyl alcohol was found 29.6% (p-NBA) and 8.3% (p-NBOH) in case of dealuminated form of HHEU zeolite, respectively. Other aromatic aldehyde, o- and m-nitrobenzaldehyde, m- and p-chlorobenzaldehyde, and benzaldehyde, were also converted by this reaction system to their respective product.

Zeolite is stable, non-toxic and preventing contamination of valuable feedstocks. Zeolite is used as heterogeneous catalyst due to cavity, its thermal stability at high temperature and selective even at unfavorable reactants ration and the reaction is eco-friendly, natural zeolites are having intercalated water molecules however after treatment of zeolite these molecules or removed and form cavity, which is responsible to the activity of zeolite. The Heulandite type studied can potentially be used in industries such as agriculture, horticulture and for environmental protection.

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