Synthesis,Characterization And Catalytic Potency Of Modified Natural Zeolites For Cannizzrao Reaction

Priya Pawaiya* Aarti Sharma, Vandana Swarnkar and Radha Tomar

Abstract-Liquid phase cannizzaro reaction of p-nitrobenzaldehyde and DMF (N, N di methyl formamide) was carried out over H-Natrolite, H-Heulandite and H-Stilbite at 80^0c. Zeolite especiallyNatrolite,Heulandite and Stilbite, effectively catalyzed the cannizzaro reaction by refluxing in DMF solvent where p-nitrobenzaldehyde was converted to p-nitrobenzoic acid and p-nitrobenzyl alcohol by self oxidation of reduction. The material was characterized by XRD (X-ray diffraction), FTIR (Fourier transform infrared spectroscopy). The various active aldehyde group compounds, such as O-nitrobenzaldehyde(O-NBAL), m-nitrobenzaldehyde, (m-NBAL), m- chlorobenzaldehyde(m-CBAL), p-chlorobenzaldehyde(p-CBAL) and benzaldehyde(BAL),were chosen the react with N, N dimethyl benzaldehyde/Acetone. P-nitrobenzaldehyde was found to be a good active aldehyde compound. The product was analyzed by gas chromatography and with FID detector. The conversion of p-nitrobenzaldehyde to p-nitrobenzoic acid (p-NBA) and p-nitrobenzyl alcohol (p-NBOH) maximum conversion was found to be 40.0% p-NBA and 10.0%p-NBOH fromof H-Natrolite zeolite comparethen Heulandite and StilbiteZeolite.

Key words- Oxidation, p-nitrobenzaldehyde,Cannizzaro reaction, zeolites, H-Natrolite, H-Heulandite and H-Stilbite.

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1. INTRODUCTION:

THE disproportionation reaction of aldehydes without α-hydrogens in presence of a strong base to furnish an alcohol and a carboxylic acid is called Cannizzaro reaction. One molecule of aldehyde is reduced to the corresponding alcohol, while a second one is oxidized to the carboxylic acid

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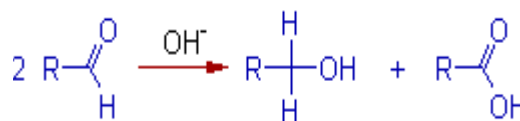
The applicability of Cannizzaro reaction in organic synthesis is limited as the yield is not more than 50% for either acid or alcohol formed. In case of aldehydes that do have α-hydrogens, the aldol condensation reaction takes place preferentially.

The α,α,α-Trihalo aldehydes undergo haloform reaction in strongly alkaline medium. e.g. Choral will give chloroform in presence of an alkali.

Zeolites are microporous,aluminosilicatem inerals commonly used as commercial adsorbents [1].Zeolites have homogeneous crystalline structures and hence shape-selective reactions using them were achieved and reported. Zeolites are crystalline hydrated aluminosilicates of the alkaline earths. Natural zeolites are formed in several geological environmental such as hydrothermal, burial melamorphic, 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[2].We have been interested in the application of zeolites to organic reactions in the liquid phase and have reported that zeolites performed the shape-selective hydrolysis of esters[3] and ring-opening reaction of epoxides[4]. Generally, aromatic aldehydes and aliphatic ones with no α-hydrogen, give the Cannizzaro reaction when treated with NaOH or other strong bases. In place of these liquid bases, 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 Natrolite type effectively catalyzed the reaction in liquid phase. Due to these properties zeolites have been found to be safe alternative for such conventional liquid acid catalysts used in synthetic organic chemistry in petroleum refining,

fine chemical synthesis and pharmaceutical industries, etc.[5-7].

Natural Zeolite are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations and consist of infinitely extending three dimensional network of $Al0_4^{5-}$ and $Si0_4^{4-}$ tetrahedral, linked by sharing of all oxygen atom. Owing to a large internal surface area and considerable costs than synthetic counterparts such as natrolite specimens have attracted researches working in the area of catalysis[8-11].

The potential use of micro porous and mesoporous catalysts in the fine chemical production is enormous[12-14]. Natrolite is a tectosilicatemineral species belonging to the Zeolite group. It is a hydrated sodium and aluminiumsilicate with the formula $Na_2Al_2Si_3O_{10} \cdot 2H_2O$[15]. The type locality is Hohentwiel, Hegau, Germany [16]. It was named Natrolite by Martin Heinrich Klaproth in 1803[17]. The crystals are frequently epitaxial overgrowths of natrolite, mesolite, and gonnardite in various orders[18].

Zeolite minerals species shall not be distinguished solely on the basis of the frameworkSi/Al ratio[19]. Individual species in a Zeolite mineral series with varying extra frameworkcations arenamed by attaching to the series name a suffix indicating the chemical symbol for theextraframework element that is most abundant in atomic properties, e.g. Heulandite-Ca,Heulandite-Na, Clinoptilolite-K, Clinoptilolite-Ca etc.

Apotential catalytic application of a pure heulandite is theisomerization of but- 1 -ene to 2-methylpropene as suggested bythe recent work of

Woo *et al.*[20]To date, synthesis of heulandites typezeolites has proven exceedingly difficult. There are tworeported synthetic routes to Heulandite. One of these requiresextreme conditions of pressure and temperature (P> 1000 atm,T > 250 ^{0}C)[21] and the other involves synthesis times of 40 to 80d.[5] additionally, several preparations of Clinoptilolite are alsogiven in the literature [22-28].Stilbite shows a wide variation in exchangeable cations (positively charged ions). Silicon, Si, ions and aluminium, Al, ions occupy equivalent sites, and can substitute for each other, but they have a different charge (Si^{4+} and Al^{3+}) so the ions occupying the Na/Ca site have to adjust to maintain charge balance. There is a continuous series between stellerite, whose formula can be written as Ca_4 ($Si_{28}Al_8$) $O72 \cdot 28(H_2O)$, and stilbite, and another a continuous series between stilbite and barrerite, Na_8 ($Si_{28}Al_8$) $O72 \cdot 26(H_2O)$. The open channels in the stilbitestructure [29-30]acts like a molecular sieve, enabling it to separate hydrocarbons in the process of petroleum refining [31].

2. EXPERIMENTAL

2.1. Catalysis and reactants

Sodium silicate (Aldrich), Aluminium nitrate, Sodium Hydroxide (Aldrich), Ammonium nitrate (Merck), Calcium nitrate (Merck), p-nitrobenzaldehyde (Himedia), DMF (N, N dimethyl formamide) were commercial sample from Merck.

2.2.Preparation of Catalysts

Zeolites Natrolite,Heulandite and Stilbite were prepared using the methods described in [33–

36].We converted them into H-form by the following procedure: Na form of zeolite and 1 M NH_4NO_3 solution (15 ml/g of Zeolite) were placed in a round-bottomed flask fitted with an air condenser. The slurry was stirred magnetically at 80 °C for 6 h and then cooled to room temperature. The material was filtered under suction and thoroughly washed with distilled water. The filtered solid material was placed in a china dish and kept in an oven at 80 °C for 12 h. The solid material was then cooled to room temperature. The dried material was once again treated with 1 M NH_4NO_3 by adopting the same procedure. The same cycle was repeated thrice in order to achieve maximum exchange of Na^+ ions. The catalyst was taken in a china dish and placed in a furnace at 550 °C for 6 h. The material was then cooled to room temperature and kept indesiccators prior to use.

2.3.Catalyst characterization

The catalysts were characterized by XRD and FTIR analysis. The elements present in the Zeolite were determined by energy dispersive X-ray 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-Kαradiation of wavelength 1.54056 Å and the diffractograms were recorded in the range 2Θ = 0° – 65° 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. 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 1cm^{-1}.

2.3. 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 range 333 K to 393 K 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 fitted with a (AT-WAX column diameter 0.25mm, thickness 0.2mm and length 30m) FID detector and qualitatively by GC-MS (Shimadzu .QP -2000). The conversion was expressed by the percentage of p-nitrobezaldehyde converted into the p-nitrobezoic 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.

Conversion % = {Initial area - final area/Initial area} x100

RESULT AND DISCUSSION

3.1. Characterization of the Catalysts
3.1.1. XRD

Powder X-ray diffraction pattern of synthesized materials was recorded at room temperature on PW 1710 diffractometer. Samples were scanned using Cu-Kα radiation of wavelength 1.54056 Å and the diffractograms were recorded in the range 2Θ= 0° – 65° at the scanning speed of 1 step /

second. The XRD pattern of Natrolite 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 Natrolite, Heulandite and StilbiteZeolite.
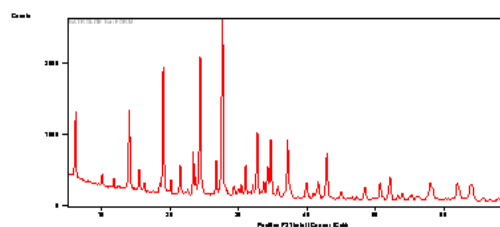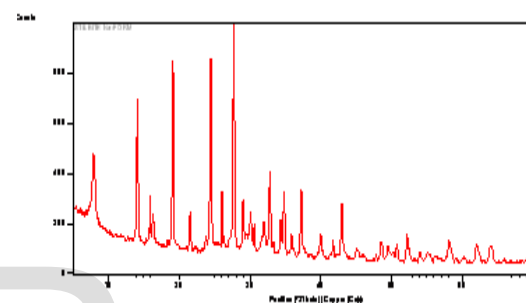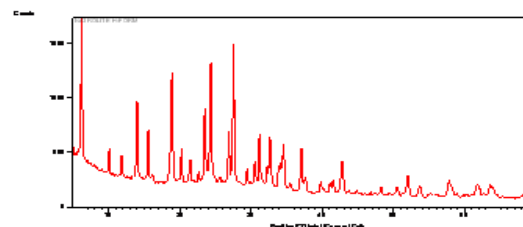

Fig:1 XRD of Natrolite zeolite
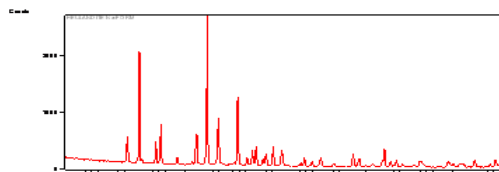

Fig:2 XRD of H- Natrolite zeolite
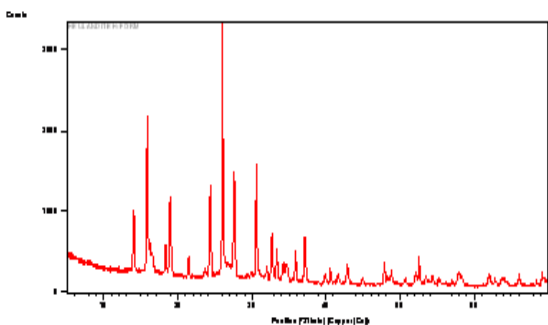
Fig:3 XRD of Heulandite zeolite

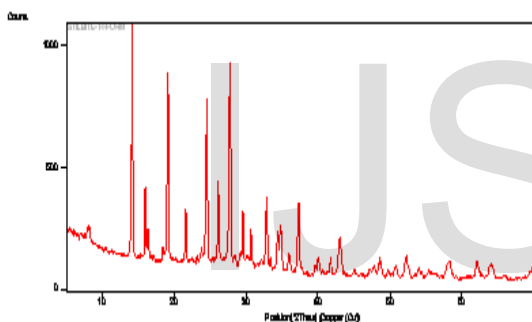**Fig:4 XRD of H-Heulandite zeolite**

Fig:5 XRD of Stlibite zeolite

Fig:6 XRD of H-Stlibite zeolite

Fig.7 FTIR spectra of p-nitrobenzaldehyde.

3.2. Catalytic activity

The catalytic activity of the calcinedNatrolite, Heulandite and Stilbite was examined in the cannizzaro reaction oxidation of p-nitrobenzoic acid and p-nitrobenzyl alcohol. The GC 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-NAT and dealuminated H-NAT, H-HEU and H- STIL catalysts.

$$Ar - CHO \frac{H - zeolite}{DMF / \mathrm{Re}\, flux} Ar - CH_2OH + ArCOOH$$

3.2.1. Effect of reaction time

The effect of crystallization time on the morphology of Natrolite, Heulandite and Stilbite type zeolites was studies in series by the synthesis performed with reference to composition of some natrolite type material in the crystallization time 10-40 hours. The increase in time and formation of larger crystals with more uniformity in partical

3.1.2. FTIR analysis

FT-IR spectroscopy was performed on SHIMADZU FTIR 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 682-820 cm-1 and 995-1118 cm-1are assigned to symmetric and antisymmetric T-O-T stretching vibration, broad band in the region of 3484 cm-1 due to asymmetric stretching of OH group and the bands at 1636 and 1384 cm-1 due to bending vibration of (H-OH) and –(O-H-O)- band respectively.

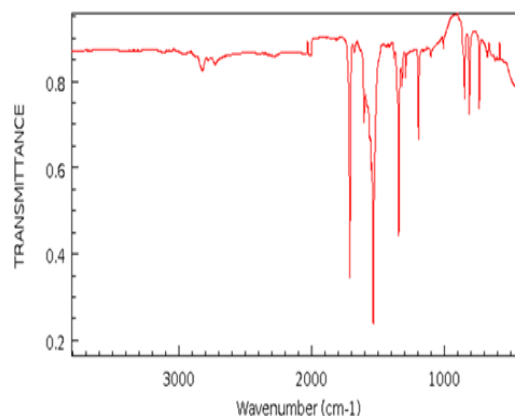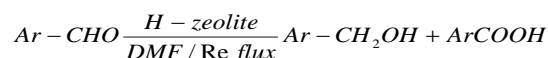size in comparison to crystals of material, synthesized at room temperature. The evolution of the characteristic data suggest than in the 10-40 hours synthesis period crystalline nature of material is observed but beyond this crystalline phase comes in to existence.

The different conversion of Heulandite and Stilbite zeolite compare to Natrolite zeolite. Fig (14).Shows theNatrolite maximum conversion 40 hours at 40% of p-nitrobenzoic acid and 10%of p-nitrobenzyl alcohol.when the time was raised to 50 hours, the conversion increased slightly for about 42.3% (p-NBA) and 11.6% (p-NBOH) .different conversion of Heulandite were shown in fig (14). It was observed that the conversion of Heulandite 40 hours at 29.6% (p-NBA) and 8.3% (p-NBOH). When time was raised to 50 to 60 hours, the conversion increased slightly about 32.3% (p-NBA) and 10.3% (p-NBOH). The same condition of Stilbite. Fig (14) shows the stilbite different conversion of Stilbite Zeolite compare to Natrolite and Heulandite. When the time for 10 hours in conversion at 18.3% and the time was raised to 40 hours. The maximum conversion is 35.6 (p-NBA) and 9.3 (p-NBOH). However it is seen that equilibration time of 40 hours. It's sufficient since maximum conversions attained during this period.
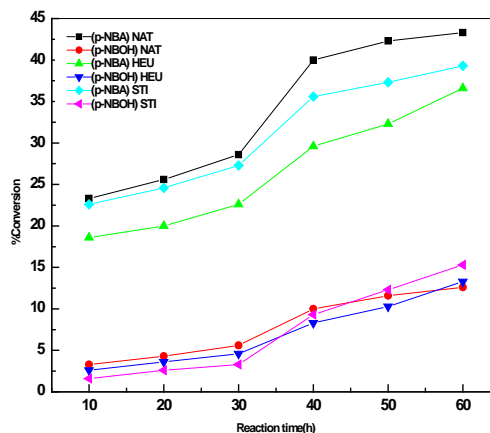

Fig.8 Effect of reaction time on conversion over Zeolites

3.2.2. Effect of molar ratio of the reactants

The effect of p-nitrobezaldehyde to DMF (di methyl formamide) molar ratio was studied at 2:1,4:1,6:1,8:1 and 10:1 by keeping the total volume constant (Fig.15). The conversion of p-nitrobenzoic acid and p-nitrobenzyl alcohol was found to increase with increase in concentration of p-nitrobezaldehyde up to eight and thereafter remained almost constant. The increasing conversion of p-nitrobenzoic acid and p-nitrobezyl alcohol. Further increase in molar ratio has no appreciable effect in p-nitrobezaldehyde and DMF conversion.
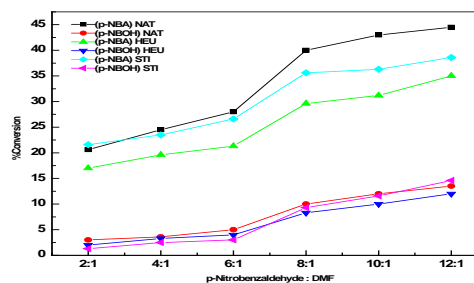

Fig.9 Effect of molar ratio of reactants on conversion of

p-nitrobenzyldehyde

3.2.3. Effect of amount of catalyst

The effect of catalyst quantity was studied over a range over of 0.010-0.060gm for benzaldehyde to p-NBA and p-NBOH at 80^0c (Fig.16). The conversion of p-NBAor 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 0.040g. This indicates that beyond 0.040g. The additional active sites do not increase the adsorption reactants and given concentration.
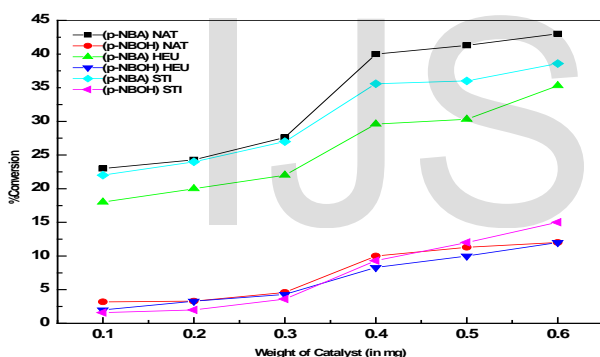

Fig.10 Effect of Catalyst loading on conversion of p-nitrobenzaldehyde

3.2.4 Effect of Reaction temperature

The effect of reaction temperature on the conversion of p-nitrobenzaldehyde was studied over a range of 50-100^0c (fig.17). The conversion was found to increase significantly with increase in temperature till 80^0c and thereafter a slight decrease was observed. (Fig.17) shows the effect of the reaction temperature on the conversion of p-nitrobenzaldehyde in to p-nitrobenzoic acid and p-nitrobenzyl alcohol over Natrolite, Heulandite and

StilbiteZeolite respectively. The conversion of p-nitobenzaldehyde 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 acid and p-nitrobenzylalcohol was found minimum in reaction period. Reaction temperature was increased 50-100^0c where we found equilibration temperature 80^0.
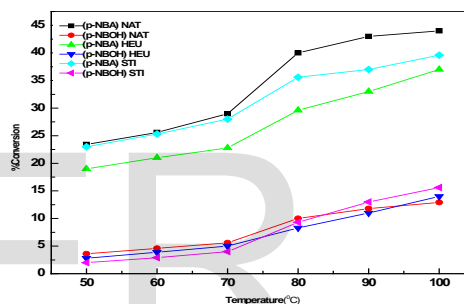

Fig.11 Effect of reaction temperature on conversion over Zeolites

4. Reaction mechanism

The cannizzaro reaction is initiated by the nucleophilic attack of a hydroxide ion to the carbonyl carbon of an aldehyde molecule by giving a hydrate anion. This hydrate anion can be deprotonated to give an anion in a strongly alkaline medium. In this second step, the hydroxide behaves as a base.
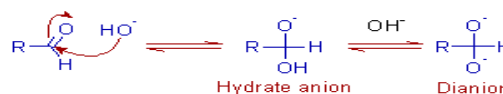
Now a hydride ion, H- is transferred either from the monoanionic species or dianionic species onto the carbonyl carbon of another aldehyde molecule. The strong electron donating effect of O- groups facilitates the hydride transfer and drives the reaction further. This is the rate determining step of the reaction.
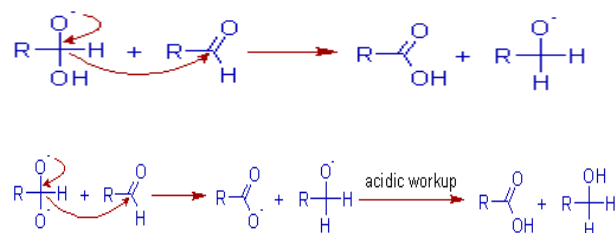
Mechanism of Cannizzaro reaction involves a hydride shift [32].

- Thus one molecule is oxidized to carboxylic acid and the other one is reduced to an alcohol.

- When the reaction is carried out with D_2O as solvent, the resulting alcohol does not show carbon bonded deuterium. It indicates the hydrogen is transferred from the second aldehyde molecule, and not from the solvent.

- The overall order of the reaction is usually 3 or 4.

- The Cannizzaro reaction takes place very slowly when electron-donating groups are present. But the reaction occurs at faster rates when electron withdrawing groups are present.

CONCLUSION:

Large pore zeolites, such as H-Natrolite, H-Heulandite and H-Stilbite, have been shown to be efficient catalysts in the cannizzaro reaction of p-nitrobenzaldehyde to p-nitrobenzoic acid (p-NBA) and p-nitrobenzyl alcohol (p-NBOH), leading to the selective formation of the corresponding p-nitrobenzaldehyde. The effect of the various experimental parameters, in particular the mole ratio of the reactants, has been studied in the reaction of p-nitrobenzaldehyde and DMF solvent over H-Natrolite Zeolite. Whatever the substrate is, H-Natrolite was generally more reactive than H-Heulandite and Stilbite zeolite an order of activity that can be directly related to the microporous structure of the different samples. It is also noticed that H-Natrolite catalyst can be reused to get good Conversion.

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