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Research Article

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Synthesis and Characterization of analogues of Zeolites and their role as catalyst in Cannizzaro Reaction of p-nitrobenzaldehyde by self oxidation and reduction

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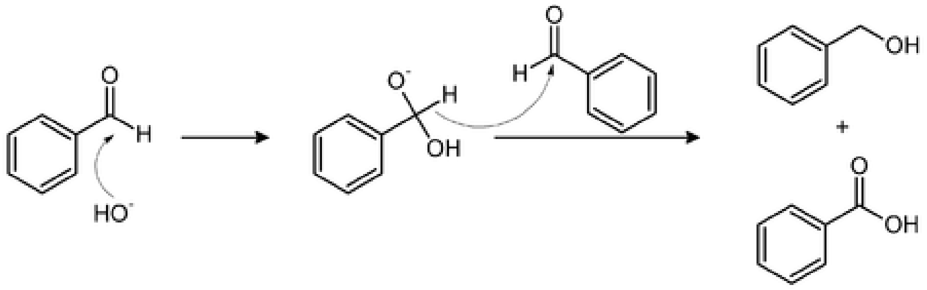
ABSTRACT

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-nitrobenzoic acid by self-oxidation-and-reduction. Natrolite was synthesized in the laboratory by hydrothermal method, after calcinations. The sample was characterized by different techniques such as powder X-ray diffraction analysis (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). 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^{0}c. The product was analyzed by Gas Chromatography and with FID Detector. The conversion of p-nitrobezaldehyde to p-nitrobenzoic acid and p-nitrobenzyl alcohol was found to be 40.0 % (p-NBA) and 10.0% (p-NBOH) form of H-Natrolite zeolite respectively.

Key words: Oxidation, p-nitrobenzaldehyde, H-Natrolite, 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[1][2]. 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. Zeolites are crystalline hydrated aluminosilicates of the alkaline earths. Natural zeolites are formed in several geological environmental 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 [3].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 [4] and ring-opening reaction of peroxides [5]. 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 H-Natrolite 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 safe alternative for such conventional liquid acid catalysts used in synthetic organic chemistry in petroleum refining, fine chemical synthesis and pharmaceutical industries, etc [6 -8].

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. Certain zeolytic frameworks are ordered, porous crystalline having a definite structure and voids, which may be interconnected by number of channel. The internal structure of these frameworks is hydrophilic. 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 [9-12].

Natrolite is a tectosilicate mineral species belonging to the zeolite group. It is a hydrated sodium and aluminium silicate with the formula $Na_2Al_2Si_3O_{10} \cdot 2H_2O$.[13] The type locality is Hohentwiel, Hegau, Germany[14]. It was named Natrolite by Martin Heinrich Klaproth in 1803[15]. The name is derived from natron, the Greek word for soda, in reference to the sodium content and lithos, meaning stone. Needle stone or needle-zeolite are other informal names, alluding to the common acicular habit of the crystals, which are often very slender and are aggregated in divergent tufts. The crystals are frequently epitaxial overgrowths of natrolite, mesolite, and gonnardite in various orders [16].

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 [17-28], phosphotungstic acid ($H_3PW_{12}O_{40}$) supported on SiO_2 in the form of Cerium salt [29], mesoporous molecular sieves such as MCM-41 [30] and clay such as montmorillolite [31] are among the solid acid catalysts that have been used in Cannizzaro reaction. The use of abovementioned 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 [32].

EXPERIMENTAL SECTION

2.1Chemicals

Sodium silicate (Aldrich), Aluminium nitrate, Sodium Hydroxide (Aldrich), Ammonium Nitrate (Merck), p-Nitrobenzaldehyde (Himedia), DMF (N, N Dimethyl Formamide) were commercial sample from merck.

2.2 Synthesis of the Catalyst (Natrolite)

Natrolite is a tectosilicate mineral species belonging to the zeolite group. It is a hydrated sodium and aluminium silicate with the formula $Na_2Al_2Si_3O_{10} \cdot 2H_2O$ [3]. 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 170^0C for 24 hours.The product was recovered by filtration, washed thoroughly with deionized water and dried at 393 K overnight, then calcined at 540^0Cfor 5 h. The Natrolite was then ion-exchanged three times with 1 M NH_4NO_3. Natrolite with Si/Al ratio of 15 was hydrothermally synthesized according to Ref. [33].

2.2 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-Kα radiation of wavelength 1.54056 Å and the diffractograms were recorded in the range $2\theta = 0^o - 28^o$ 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 $1cm^{-1}$.

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 rang 80^0c 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 0.25mm, thickness 0.2mm and length 30m) FID detector and qualitatively by GC (Shimadzu). 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

2.3.1 Reaction procedure

A typical example of Cannizzaro reaction of p-nitrobenzaldehyde is illustrative; Zeolite Natrolite (0.040g) and its H-form are used as catalyst in this reaction. P-nitrobenzaldehyde (0.378g) was added in 10 ml of (DMF solvent) in flask and the suspension was refluxed with magnetic stirrer for 40h at 80^0c temperature. Aliquot of reaction mixture was analyzed by gas chromatography (GC).

2.3.2 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 SN^2 mechanism.

RESULTS AND DISCUSSION

3.1 Characterization

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 $2\theta = 0^o - 5^o$ at the scanning speed of 1 step / second. The XRD pattern of Natrolite Zeolite samples (Sodium form and Hydrogen form) are shown in Fig. (1-2). the peaks are characteristic of Natrolite zeolite which was compared to the diffraction pattern of Natrolite Zeolite.

3.1.2 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.3 shows the peaks between 682-820 cm-1 and 995-1118 $cm^{-1}$are 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.

3.2 Catalytic activity

The catalytic activity of the calcined Natrolite 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-Natrolite and dealuminated H-Natrolite catalysts.

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

3.2.1 Effect of reaction time

The effect of crystallization time on the morphology of Natrolite zeolite was studies in series by the synthesis performed with reference to composition of some Natrolite 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 80^0c 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. Natrolite zeolite. Fig (6). Shows the Natrolite 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). Its sufficient since maximum conversion is attained during this period.for further study the reaction time fixed as 40hrs.

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.7). The conversion of p-nitro benzoic acid and p-nitro benzyl 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.

3.2.3 Effect of amount of catalyst

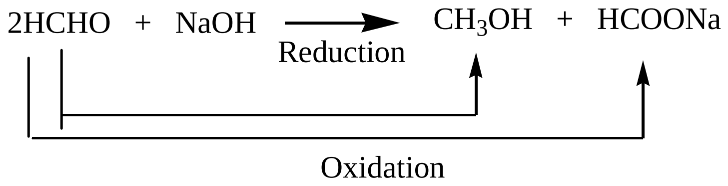
The effect of catalyst quantity was studied over a range over of 0.010-0.060g for benzaldehyde to p-NBA and p-NBOH at 80^0c (Fig.8). The conversion of p-NBAor p-NBOH was found to increase with increase in catalyst amount which is due to the proportional increase in the number of active sites and then 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.

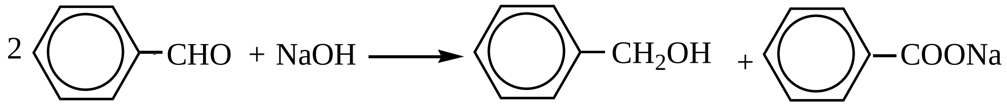
3.2.4 Effect of reaction temperature

The effect of reaction temperature on the conversion of p-nitrobenzaldehyde was studied over a range of 50-100^0c (fig.9). The conversion was found to increase significantly with increase in temperature till 80^0c and thereafter A slight decrease was observed.

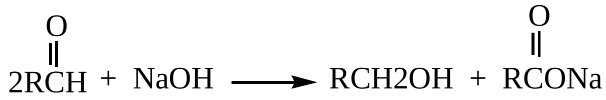
(Fig.9) shows the effect of the reaction temperature on the conversion of p-nitrobenzaldehyde in to p-nitrobenzoic acid and p-nitrobenzyl alcohol over Natrolite zeolite respectively. The conversion of p-nitobenzaldehyde increased with the reaction temperature over these Zeolites. The equilibration temperature was calculated by these data where the conversion distance of p-nitrobenzaldehyde into p-nitrobenzzoic and alcohol was found minimum in reaction period. Reaction temperature was increased 50-100^0c where we found equilibration temperature 80^0c.

4. Reaction mechanism



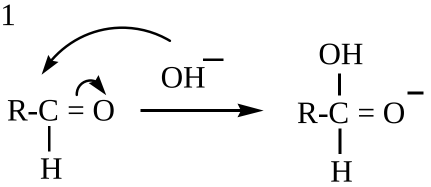


Mechanism:



$$2RCH(=O) + NaOH \longrightarrow RCH2OH + RC(=O)ONa$$

STEP- 1



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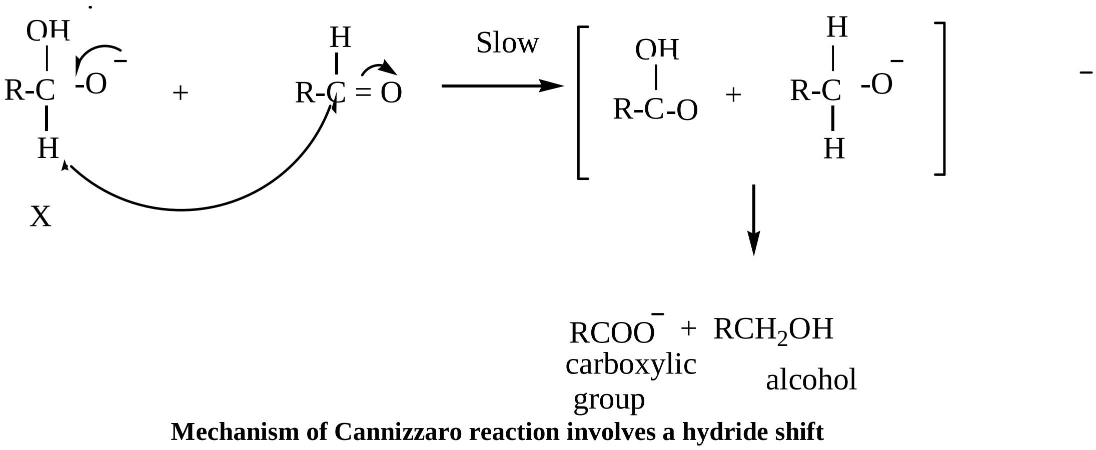

Mechanism of Cannizzaro reaction involves a hydride shift

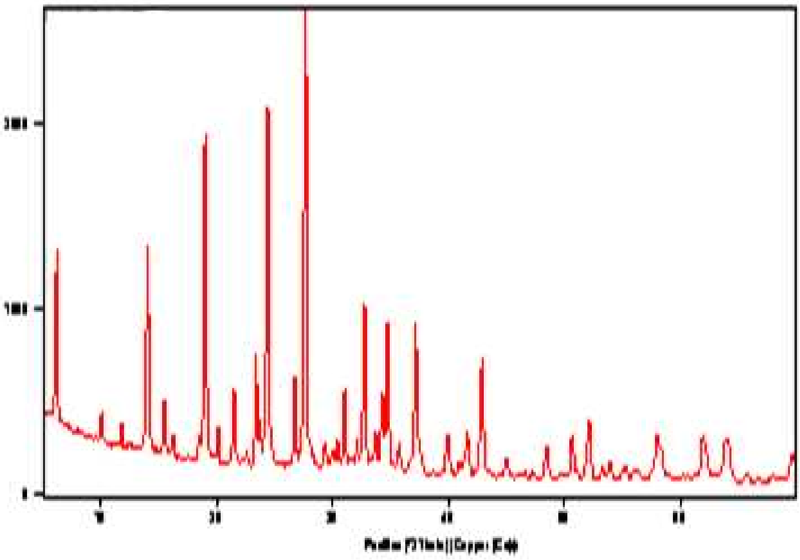

Fig:1 XRD of Natrolite zeolite

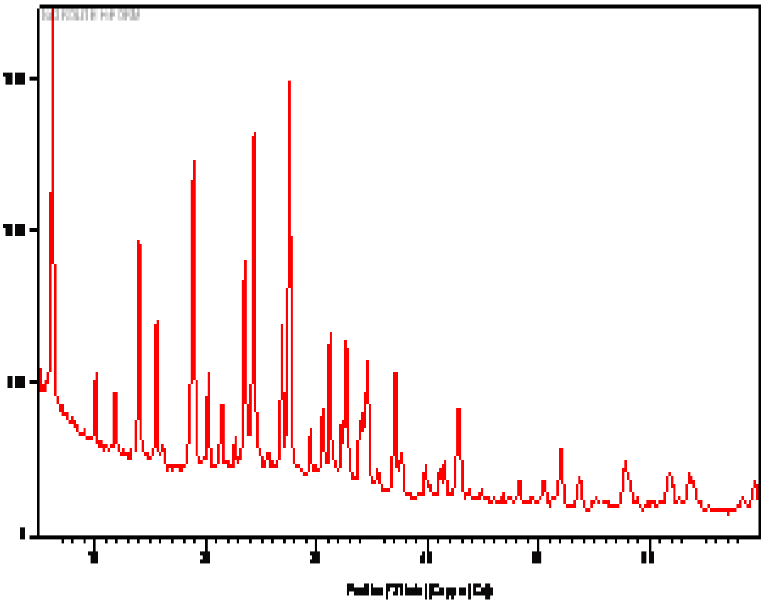

Fig:2 XRD of H- Natrolite zeolite

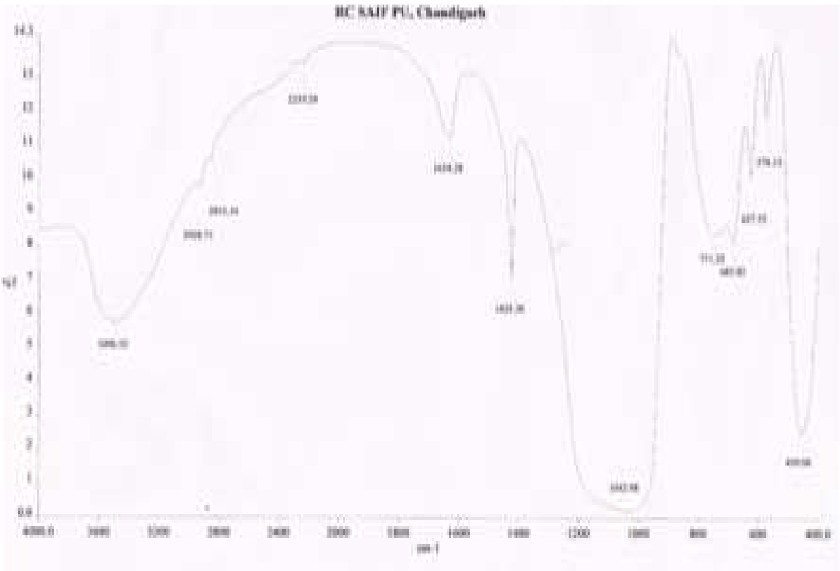

Fig-3 FTIR spectra of Natrolite zeolite

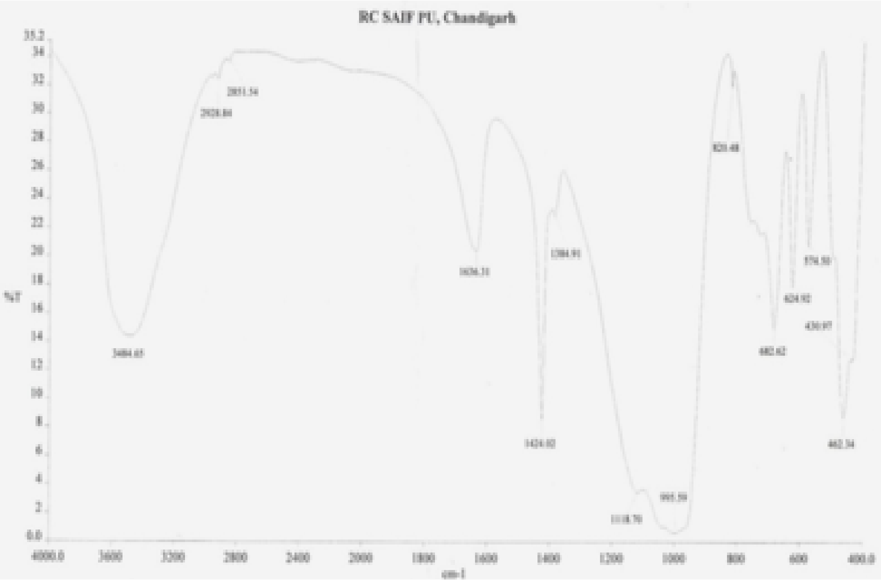

Fig-4 FTIR spectra of H- Natrolite zeolite

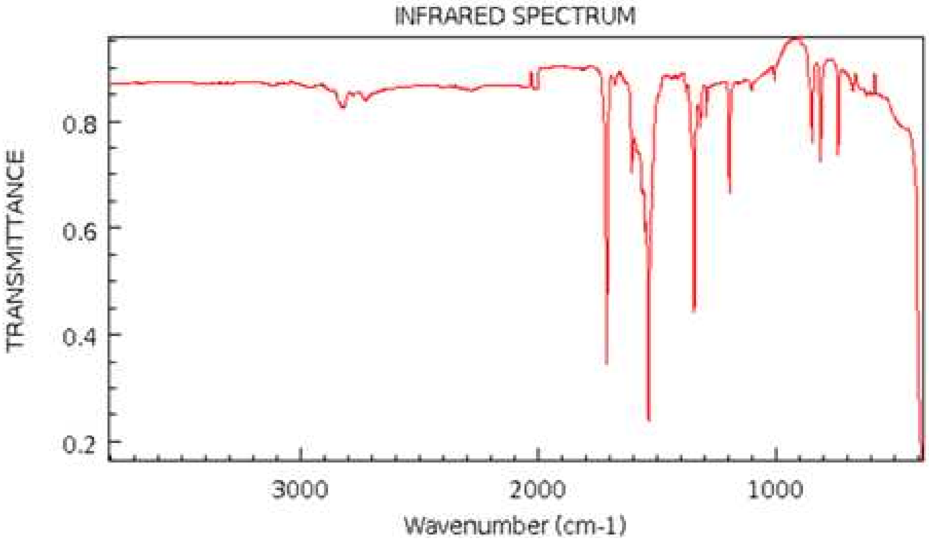

Fig.5 FTIR spectra of p-nitrobenzaldehyde

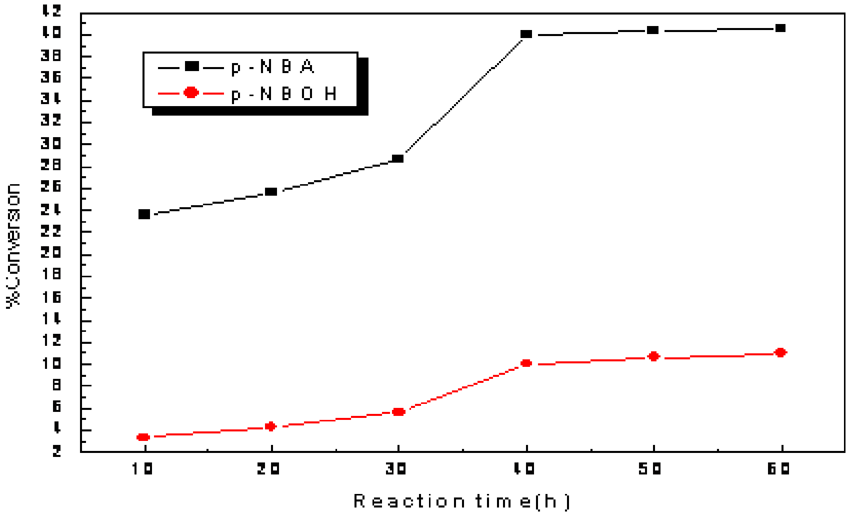

Fig.6 Effect of reaction time on conversion over Natrolite

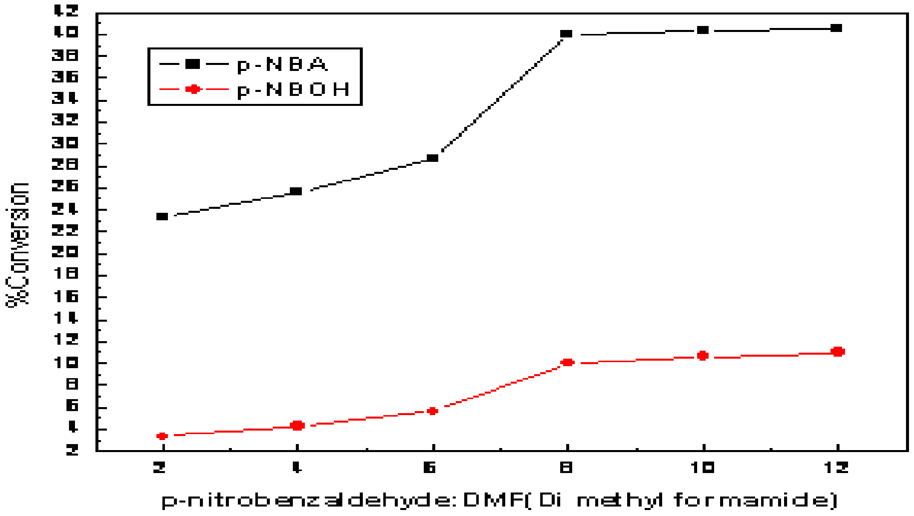

Fig.7 Effect of molar ratio of reactants on conversion of p-nitrobenzyldehyde

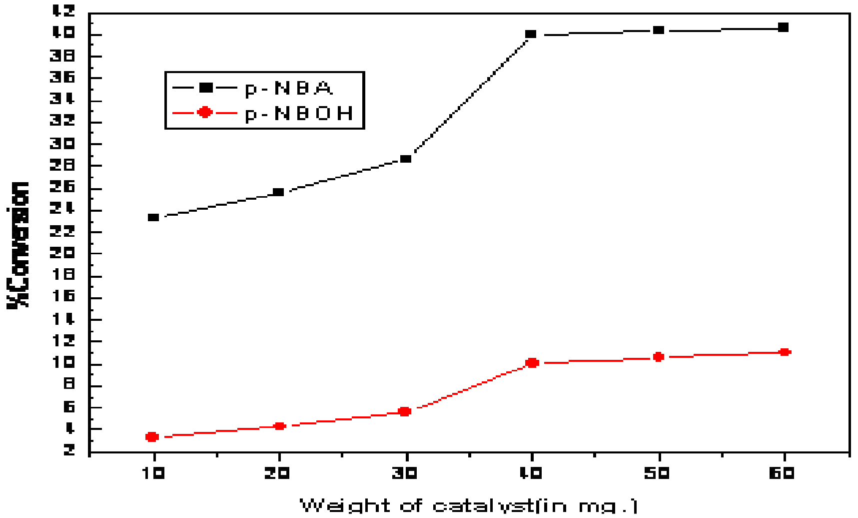

Fig.8 Effect of Catalyst loading on conversion of p-nitrobenzaldehyde

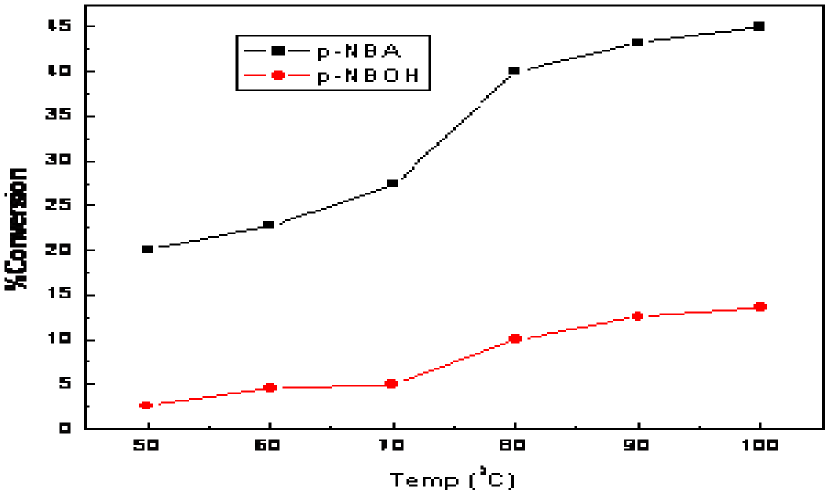

Fig.9 Effect of reaction temperature on conversion over Natrolite

CONCLUSION

The present work deals with the synthesis of zeolites Natrolite, 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-nitrobezaldehyde 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 p-nitrobezaldehyde to p-nitrobenzoic acid and p-nitrobenzyl alcohol. Under the optimum reaction conditions (p-nitrobezaldehyde : p-NBA and p-NBOH mole ratio of 8:1, and reaction time for 40hrs) conversion of p- nitrobezaldehyde to p-nitrobenzoic acid and p-nitrobenzyl alcohol was found 40% and 10% in case of dealuminated form of HNAT zeolite respectively.Other aromatic aldehyde, O-and m-nitrobezaldehyde, m-and p-chlorobezaldehyde, 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 intercalculated water molecules however after treatment of zeolite these molecules or removed and form cavity which is responsible to the activity of zeolite.

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