



NANOZEOLITE SPUR ASSISTED SYNTHESIZED BETA-BENZOYL PROPIONIC ACID BY ULTRASONICATION ASSORTMENT

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Abstract

In recent study Zeolite has remarkable uses for their applications in organic synthesis. Green approach towards synthesis of 1-phenyl naphthalene and their derivatives from β benzoyl propionic acid (β -BPA) in few segments. Precursor β -BPA prepared followed by Friedel craft reaction using green reagent such as Nanozeolite. It is crystalline, sodium aluminum silicate hydrate hydrochloride on treatment with β – TEA replacement for anhydrous aluminum chloride. In conventional method, benzene and succinic anhydride are condensed with activated Nanozeolite and for work-up in reaction to gives desired product followed by re- cyclization of catalyst. Ultrasonication induced synthesis of β -BPA it lessened to two stages on firstly acylation by using Ultrasonication irradiation with activated nanozeolite and in second step hydrolysis followed by re-cyclization of catalyst. It has been observed that sonication method creates better yield, reduces reaction time and energy compared with conventional synthesis lignans.

Keywords: β benzoyl propionic acid, sodium aluminum silicate hydrate, sodium aluminum silicate hydrate, Ultrasonication irradiation, nanozeolite.

1 Introduction

Green approach towards synthesis of 1-phenyl naphthalene involves key precursor like beta benzoyl propionic acid. The β -Benzoyl propionic acid have been synthesized followed by Friedel Craft reaction by many ways like general method like benzene, succinic anhydride and $AlCl_3$. It is replaced by green methods as Ultrasonication using $AlCl_3$, conventionally and Ultrasonication using Nanozeolite zeolite catalyst. In one of the several methods used for the synthesis of 1-phenyl naphthalene type of lignan, Haworth and co-workers prepared the system in a series of steps by starting with β -Benzoyl propionic acid. In 1877 Charles Friedel and James Crafts developed a conventional of reactions to attach substituent's to an aromatic ring named as Friedel–Crafts reaction [1]. Friedel–Crafts reactions known as alkylation and acylation reactions together advance by electrophilic aromatic substitution reactions [2]. In which alkylation may give poly alkylated products, consequently the FC acylation is a treasured atom economy alternative. The acylated producing molecule easily is transformed to the resultant

alkanes followed by Wolff-Kishner Reduction or Clemmensen Reduction. It is the acylation of aromatic rings with a succinic anhydride using a strong Lewis acid catalyst. It is furthermore probable with acid chlorides and cyclic anhydrides [3-5]. This reaction partake several advantages over the FC alkylation reaction. Ketone product be situated constantly less reactive than the original molecule, so multiple acylation do not occur due to the electron-withdrawing effect of the carbonyl group. There are no carbocation rearrangements, as the carbonium ion is stabilized by a resonance structure in which the positive charge is on the oxygen as shown in figure 1.

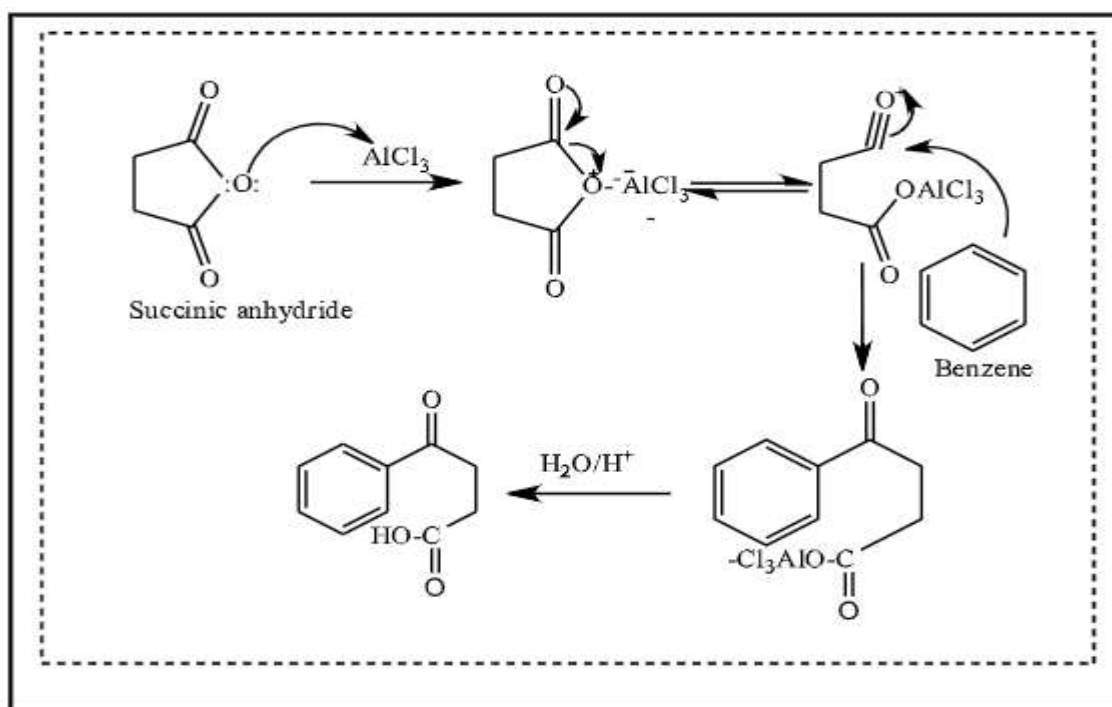


Figure 1: Mechanism of Synthesis of β -Benzoyl propionic acid using catalyst (anhyd. AlCl_3)

FC acylation's of benzene derivatives such as anisole, toluene, and naphthalene are acylated through acetic anhydride and it was investigated in the liquid phase using the Nanozeolite [6-7]. Moreover the most active catalyst as nanozeolite for acylation reactions compared to anhydrous AlCl_3 . Precincts caused by mass transfer to convert it into coke deposition. There are two types of coke (extractable and non-extractable) were notorious [8-12]. Conjoining those liquid phase reaction with continuous extraction of the catalyst vsuch as nanozeolite with refluxing reaction

mixture in a sox-let reactor headed to a sophisticated renovation of β -benzoyl propionic acid and their derivatives [13-16]. Nanozeolite has been optimized for acylation processes [17-22]. In the acylation of Benzene, toluene, and with acetic anhydride and Nanozeolite of low Si/Al charter ratio show enriched commotion and sluggish deactivation[23-30]. FC acylation of naphthalene with acetic anhydride the discerning delamination of the peripheral superficial of a Nanozeolite augments the contour exercising judgment to the nanozeolite, amassed the fussiness to the fewer statically hindered and firm products such as β -Naphthoyl propionic acid[31-33]. To conclude, the rheostat of the route circumstances is vital in the case of the hydrolysis with mineral acid and cold water treatment via cold sodium carbonate to form desired products [34-39]. In case of friedel craft reaction, when benzene and succinic anhydride on treatment with Lewis acid such as anhydrous $AlCl_3$ is replaced by Nanozeolite[40-43].

1.1 Rice Husk

Rice husks are the hard protective coverings of rice grains, which are isolated from the grains during the milling process. The elemental constitution (wt%) of rice husk is 41.92% C, 6.34% H, 1.85% N, and 0.47% S. The proximate analysis (wt%) of rice husk is 10.89 moisture, 73.41 volatiles, 11.44 fixed carbon, 15.14 ash, and 12.87 HHV (MJ/kg). The main impurities in RHA are K_2O and Na_2O , and their levels are related to the type of soil and fertilizer amount used during the process of plant development.



Figure 2: Definite Rice Husk material



Rice husk is an agricultural waste generated in massive quantities from rice-processing units worldwide. With no worthwhile use, it is a waste material that creates disposal problems. Its high silica content makes it suitable for use with cement, zeolite synthesis.

Rice plants absorb silicon (Si) from soil solution in the form of monosilicic acid, also called orthosilicic acid (H_4SiO_4). Plants absorb orthosilicic acid released from silicates and polysilicic acids, even though plants can utilize silicon in both forms. Silica as a beneficial element for plant may reduce biotic and abiotic stresses. Silicon has been recognized as for reducing rice blast caused by fungus *Magnaporthe grisea* (Winslow et al 1997; Meena et al 2004) and enhancing wheat resistance to freezing stress (Liang et al 2008). Rice straw contains 86% of total silicon storage in rice plants. Rice is Si accumulator plant that has physical-chemical functions for plant growth. The rice husk, also called rice hull, is the coating on a seed or grain of rice. It is formed from hard materials, including silica and lignin, to protect the seed during the growing season. Each kg of milled white rice results in roughly 0.28 kg of rice husk as a by-product of rice production during milling.

1.2 Component

Rice husk constitutes about 20% of the weight of rice and its composition is as follows:

- Cellulose 50 %
- Lignin 25-30 %
- Silica 15-20 %
- Moisture 10-15 %

The rice husk renewable waste contains 28-30% of inorganic and 70-72% of organic compounds.

1.3 Chemical composition

Produced during rice milling, the rice husk is already dried and accumulated at the factory. The



specific weight of uncompressed rice husk is about 100 kg/m³. Average properties of rice husk in proximate analysis a and ultimate analysis b are shown in Tables 1 and 2, respectively, according to various research on the rice husk by Beagle (1978), Jeng et al. (2012), and Jenkins (1998).

Table 1: Rice Husk composition in % weight (dry basis) based on proximate analysis.

Fixed carbon (%)	Volatile matter (%)	Ash (%)
11.4	73.41	15.41

**Table 2:
Composition
of Rice
Husk in %
weight (dry
basis) based
on ultimate
analysis.**

C %	H %	O %	N %	S %	Ash %	HHV (MJ/kg)
40	5	34.8	0.8	0.1	19.5	14.8

1.4 Regional Composition

The variability of composition and characteristics of rice is really broad and depends on variety and environmental conditions under which the crop is grown. In husked rice, protein content ranges in between 7 % to 12 %. The use of nitrogen fertilizers increases the percentage content of some amino acids.

The silicon content of rice grain collected from the region ranged from 1.20 to 5.99 per cent with an average value of 3.01 per cent, respectively and the rice straw Si content varied from 3.52 to 9.80 per cent with an overall mean of 6.30 per cent of different districts.

1.5 Nanozeolite

M. Cambor and P. Pariente were firstly identified the multifunctional material named as Zeolite. Moreover verified by Xianping Meng, Shu-Hua Chien, D. Cardoso and S. Jahn to various catalytically reforms. The crystalline composition of Nanozeolite material $\text{Na}_{0.92} \text{K}_{0.62} (\text{TEA}) [\text{Al}_{4.53} \text{Si}_{59.47} \text{O}_{128}]$ and Batch Composition without interlayer material

1.97 Na_2O : 1.00 K_2O : 12.5 : (TEA) 20 : Al_2O_3 : 50 SiO_2 : 750 H_2O : 2.9 HCl .

The tetraethyl ammonium-Beta (TEA- β) Nanozeolite used in this work have been synthesized following the procedure described in the literature [44-47]. Si:Al ratios of samples in between 7 and 106 (as measured by chemical analysis) and their limpid proportions in the range of 0.2-0.9 μm (as measured in scanning microscopy) were acquired. The acid form of these nanozeolites were synthesized in the resulting in way TEA-3 samples were heated at 550°C for 3 hours by sluggishly accumulative the heating in absence of oxygen having temperature (5°C min^{-1}), with one-hour halfway periods at 350 and 450°C . Subsequently this behavior all TEA fragments taken remained uninvolved on or after the zeolite (as supervised by IR spectroscopy). In a second step, the zeolite was exchanged with 1 M ammonium acetate solution and then impassioned at 550°C for 3 hours as designated.

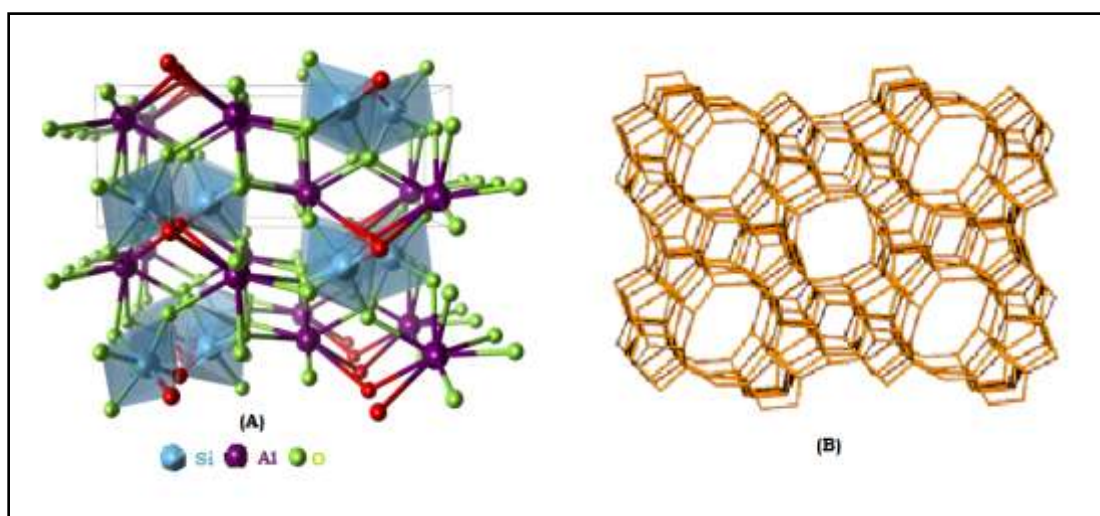


Figure 3: A) Framework and B) Three dimensional skeleton of Nanozeolite



2. Experimental section

2.1 Reagents and analysis

All the chemicals and reagents were LR, SR and AR grade and produced from Ee. Merk, (India), LOBA Chemie, Sigma-Aldrich (USA), Mumbai, Central Scientific (Nagpur). FTIR spectra were recorded on brucker. ¹HNMR were recorded on 400MHz Brucker spectrometer in CDCl₃ as solvent and TMS as an internal standard. Melting points were recorded at oil bath of thermo-fisher melting point apparatus. Analytical TLC was performed on glass slides coated of silica gel G per UV-254 of 0.2 mm thickness. Mass spectra using. For conventional experiments described below as magnetic stirrer was used. For the Ultrasonication irradiation experiments, house hold Ultrasonication oven equipped with a turn able was used (Elapsed time indicator displays duration of sonication, Overload protection, Overload protection, RoHS compliant: lead free components, Standard for cell disruption, DNA/RNA shearing and homogenization, Voltage: 110 V, Design: Benchtop, Controls: Digital, Frequency Output: 20 kHz, Pulse Mode Operation, Cooling Method: Cup Horn, Probe Diameter: 0.125", Order Separately, Probe Type: Generator, Wattage Output: 125 W, Manufacturer SKU: Q125-110, Q125A-110

2.2 Materials

Succinic anhydride, aluminum chloride (AlCl₃), benzene, naphthalene, toluene, anhydrous sodium carbonate, concentrated hydrochloric acid, sodium chloride, sonicator, the rice husk was collected from Naidu Rice Mill, Umrer Dist- Nagpur.

2.3 Synthesis of Nanozeolite:

2.3.1 Conversion of rice husk to Rice Husk Ash

Rice husk ash (RHA) is an abundantly available and renewable agriculture by-product from rice milling in the rice-producing countries. It has the highest proportion of silica content among all plant residues.



Figure 4: Rice husk ash (RHA)

It is a product of incineration of rice husk. Rice husk ash (RHA) can be obtained by pyrolyzing the RH at temperatures ranging from 500 °C to 800 °C for 5–6 h in a muffle furnace (Carbolite) to remove the organic contents. Amorphous silica is the major constituent of ash whose reactivity is attributed to the presence of this form of silica and to its very large surface area resulting from the microporous structure of ash particles. The average composition of well-burnt RHA is 90% amorphous silica, 5% carbon, and 2% K₂O. The yield of silica in this sample ash was 89.00%. Silicon oxide forms the main component of the ash with trace amounts of Al₂O₃, Fe₂O₃, CaO, MgO, K₂O, and Na₂O.

The ash of rice husk contains approximately 9.0% silica, which is a highly porous structure and is lightweight, with high specific surface area. Rice husk ash has been applied as an additive in many materials and applications, such as refractory brick, manufacturing of insulation, and materials for flame retardants. This is due to its highly porous structure and its good insulating property. The properties of rice husk ash silica vary according to the firing temperature and time.

Most of the evaporable component of rice husk are slowly lost during burning and primary residues are the silicates. Characterization of ash are dependent on:

- ❧ Composition of rice husk
- ❧ Burning Temperature

☞ Burning Time

☞ Availability of oxygen (aerobic or anaerobic)

Under controlled burning conditions, the volatile organic matter in the rice husk consisting of cellulose and lignin are removed and the residual ash is predominantly amorphous silica with a (microporous) cellular structure. Due to its highly microporous structure, specific surface area of RHA as determined by the Brunauer–Emmett–Teller (BET) nitrogen adsorption method can range from 20 to as high as 270 m²/g, while that of silica fume, for example is in the range of 18–23 m²/g.

The obtained chemical compositions of rice husk ash are tabulated in table given below:

Table 3: Chemical Compositions of Rice Husk Ash

Content, % wt.							
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅
93.4	0.05	0.06	0.31	0.35	1.4	0.1	0.8



Figure 5: Crystalline outlook of Zeolite

Zeolites are inorganic materials with regular microporous structure which have been widely developed and used in many applications. The structure of zeolite consists of the network of tetrahedral [SiO₄]₄ and [AlO₄]₅. These tetrahedrons are linked through oxygen-



spherical bonds to form an open structure with empty holes. Many types of zeolite such as zeolite X, A, P1, Y or ZSM-5 have been successfully synthesized from commercial silica sources or wastes with high silica content. Zeolite X which belongs to the faujasite (FAU) family with large pore size (about 8\AA) possessed special properties in the adsorption of heavy metals, gas or organic wastes. Zeolite X has been synthesized using silica sources such as kaolin, bauxite, diatomite, bagasse fly ash, coal fly ash, and RHA.

Zeolites can be synthesized from different raw materials which can be either natural or man-made. However, all raw materials are not suitable for synthesizing the zeolite from the economic point of view. Hence, raw materials should have some properties. They should be cheap, readily available, low production cost, selectivity, high production yield, and less abundance of foreign substances.

Synthetic zeolites have versatile applications ranging from the environmental to medicinal applications. Hence, more emphasis is given on the basic understanding of the chemistry of zeolite structures and different routes of preparations. Apart from this, many attempts have also been given on the use of different sources of raw materials in order to get a suitable zeolite having versatile properties. But, the main parameter is the proper content of the alumina and silica in the raw materials.

Table:4: Advantages and disadvantages of rice husk ash for producing synthetic zeolites

Raw Material	Chemical Composition %	Advantages	Disadvantages	Synthesis Route	Zeolite
Rice Husk Ash	80% silica, Al ₂ O ₃ , iron oxide, CaO, MgO, sodium and potassium oxides, and others	Low cost, ultrafine size, highly porous and chemically reactive.	Pre-treatment of RHA and waste glasses increase the cost.	Hydrothermal	ZSM5, T, NaY

The RHA is a residue rich in amorphous silica, and it is very active in the synthesis of zeolite. The chemical analysis reveals that RHA contains 90%–99% of silica. RHA is very cheap which can be used in several industrial sectors. Meanwhile, RHA is well-known as a rich source of

silica (about 90%) and is an excellent source for the synthesis of zeolite, silica and cordierite. Zeolite synthesis from RHA opens a new route in alleviating environmental pollution caused by RHA. Zeolites are porous crystalline silicates with a complex crystallographic structure giving rise to specific molecule-sized pores. Zeolites are widely used as catalysts and sorbents. Certain advantages and disadvantages of rice husk ash for producing synthetic zeolites are tabulated below. Steps involved in the synthesis of zeolite from rice husk are as follows:

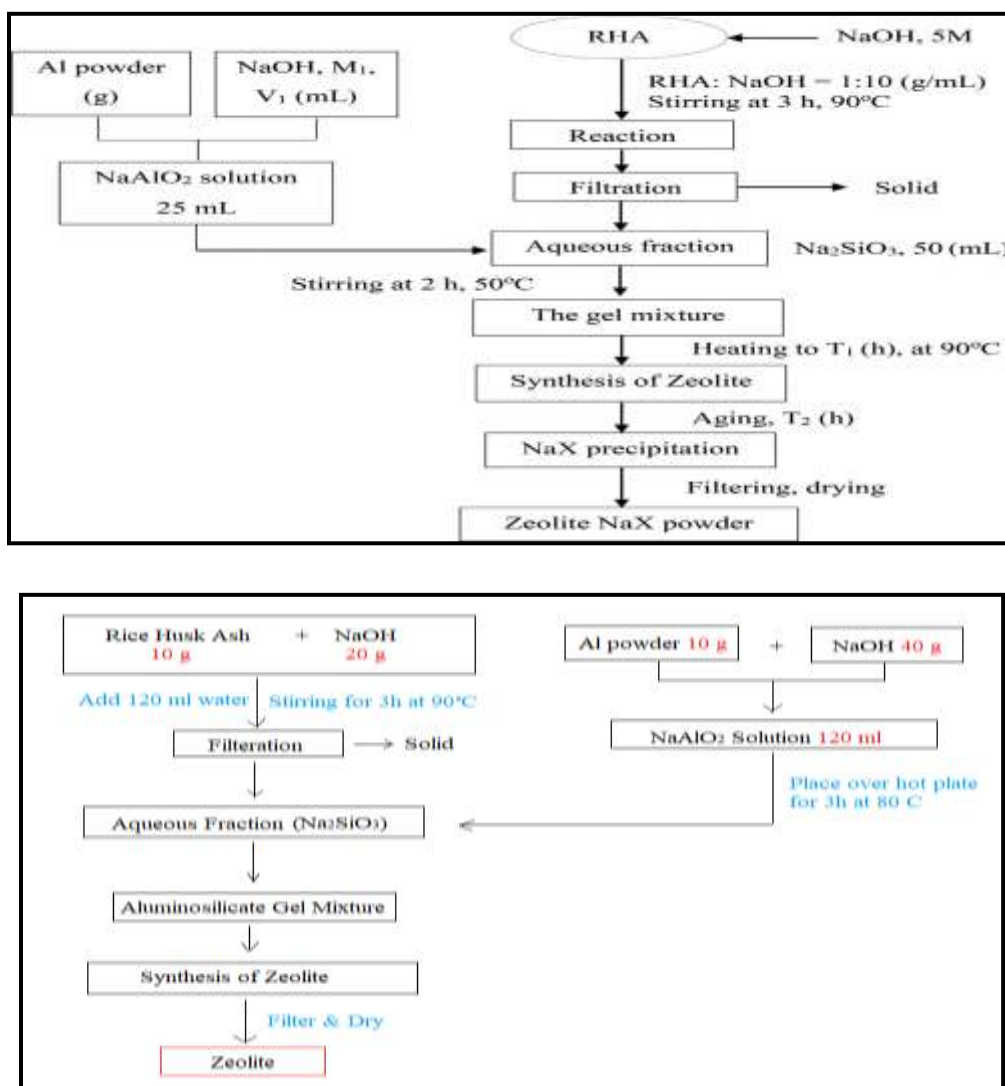


Figure 6: Flowchart of zeolite NaX synthesis process

2.3 Synthesis of Beta Benzoyl propionic acid

Ultrasonication induced organic synthesis (UIOS) followed by Friedel Craft acylation reaction. The use of Nanozeolite as an acid catalyst provides a useful alternative to the known methods for replacement of anhydrous AlCl_3 in Friedel–Craft Reaction. Short reaction time, mild conditions, high yield, less amount of catalyst, and the recyclability of used catalyst are notable advantages.

2.3.1 Activation of catalyst by using Autoclave

The Nanozeolite is a shape selective catalyst for their better activity it required activation by autoclave. Autoclave has principle to sensitize the material like zeolite at 121°C , a 15 lbs pressure for 45 minute. Firstly the material has poured in phytoplasic polymer jar (thermoplastic- which resist from heat) and autoclaved with above said conditions.

2.3.2 Preparation of β - benzoyl propionic acid

β -benzoyl propionic acid has prepared from succinic anhydride, benzene and activated Nanozeolite. (Figure 4.9)

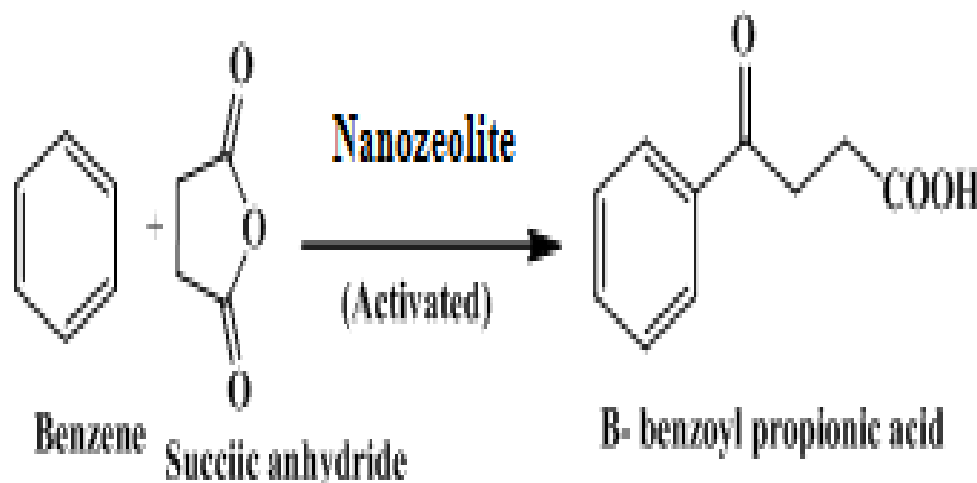


Figure 7: Green Method for synthesis of β -benzoyl propionic acid via Nanozeolite

In a 2 L three-necked round bottom flask fitted with a mechanical stirrer and two reflux



condensers are placed 68g (0.68 mole) of succinic anhydride and 350 g (4.5 mole) dry, thiophene free benzene. With continuous stirring is started and 100 g (1mole) of crystalline, activated Nanozeolite zeolite (It acts as highly reactive hydrogen abstractor) is added all at once. Hydrogen chloride fumes are evolved and the mixture becomes hot. the flask is then surrounding by cold water and 300 cc of water is slowly added from a dropping funnel inserted in the top of condensers the excess of benzene is discarded and obtained mass separates as a colorless oil which soon solidifies after cooling to 0⁰C, it is collected, washed with a cold mixture of 50 cc of concentrated hydrochloric acid and 150 cc of water. The crude β -BPA is dissolved in a solution of 75 gm of anhydrous sodium carbonate in 25 cc of water by boiling for fifteen minutes. The clear colourless filtered is transferred to 500 cc of beaker and carefully acidified with 6.5 cc of concentrated hydrochloric acid in freeze condition to maintain temperature 0-5⁰C by ice-salt bath. The solution is filtered by suction pump, washed with hot water, dry give β -benzoyl propionic acid. Repeat finally those compounds are characterized by IR, NMR and mass spectra.

2.4 Ultrasonication irradiation: Nanozeolite assisted

The irradiation of a liquid sample with ultrasonic (>20 kHz) waves resulting in agitation. Sound waves propagate into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. Sonication is the act of applying sound energy to agitate particles in a sample, for various purposes such as the extraction of multiple compounds from plants, microalgae and seaweeds. Ultrasonic frequencies are usually used, leading to the process also being known as ultrasonication or ultra-sonication. It is in field of science innovation and green technology in which conventional method is replaced n method such as ultrasonication induced organic synthesis (UIOS) of β - benzoyl propionic acid.

Ultrasonication induced organic synthesis (UIOS) of β - benzoyl propionic acid by using Nanozeolite. In case of friedel craft reaction, when benzene and succinic anhydride on treatment with Nanozeolite under Ultrasonication irradiation [19-20]. In Ultrasonication method reduce reaction time with optimum temperature to increase yield of desired product.

2.4.1 Preparation of β - benzoyl propionic acid

β -benzoyl propionic acid has prepared from succinic anhydride, benzene and activated Nanozeolite. In a 2 L three-necked round bottom flask fitted with a mechanical stirrer and two reflux condensers are placed 68 g (0.68 mole) of succinic anhydride and 350 g (4.5 mole) dry, thiophene free benzene. With continuous stirring is started and 200 g (1.5 mole) of powdered, anhydrous aluminium chloride (It acts as highly reactive hydrogen abstracter) is added all at once. Hydrogen chloride fumes are evolved and the mixture becomes hot. the flask is then surrounding by cold water and 300 cc of water is slowly added from a dropping funnel inserted in the top of condensers the excess of benzene is discarded and obtained mass separates as a colorless oil which soon solidifies after cooling to 0°C, it is collected, washed with a cold mixture of 50 cc of concentrated hydrochloric acid and 150 cc of water. The crude β -BPA is dissolved in a solution of 75 gm of anhydrous sodium carbonate in 25 cc of water by boiling for fifteen minutes. The clear colourless filtered is transferred to 500 cc of beaker and carefully acidified with 6.5 cc of concentrated hydrochloric acid in freeze condition to maintain temperature 0-5°C by ice-salt bath. The solution is filtered by suction pump, washed with hot water, dry give β -benzoyl propionic acid. Repeat finally those compounds are characterized by IR, NMR and mass spectra.

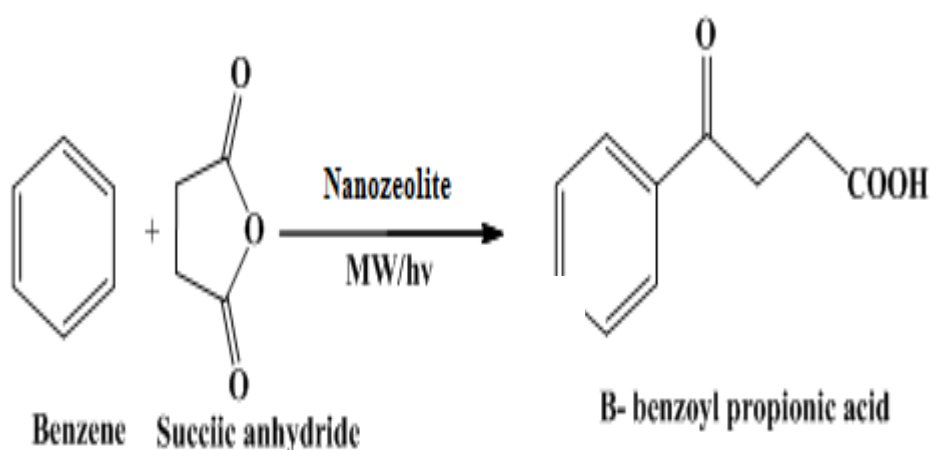


Figure 8: Ultrasonication assisted synthesis of β -benzoyl propionic acid via Nanozeolite

3. Result and discussion:

3.1 Comparative study between anhydrous $AlCl_3$ and Nano

In Friedel-Craft reaction, β -benzoyl propionic acid has been prepared by conventionally and by sonicated irradiation. Blending of benzene and succinic anhydride are treated with lewis acid such as anhydrous $AlCl_3$ is replaced by zeolite Nano. The Nanozeolite act as lewis acid. The derivatives of β -benzoyl propionic acid are prepared by series of benzene, toluene and naphthalene underwent with succinic anhydride using anhydrous $AlCl_3$ or Nanozeolite catalyst.

Table 1: Comparative study of Catalysts anhydrous $AlCl_3$ and Nano For synthesis of β -benzoyl propionic acid

SN	P	Molecular Formula	Time (Min)		Yield (%)		Anhydrous $AlCl_3$		Nano Zeolite	
			CV	US	CV	US	CV	US	CV	US
1	2a	$C_{10}H_{10}O_3$	45	5	30	3.23	76	86	88	90
2	2b	$C_{11}H_{12}O_3$	38	4.2	22	1.34	80	88	91	92
3	2c	$C_{14}H_{12}O_3$	12	2.15	08	.28	82	89	93	94

3.2 X-ray Powder Diffraction

XRD has taken as a measure of the crystal lenity of a nanozeolite sample in different phases with Si/Al=10, variation of the area under the main peak ($2\theta=22.4$) as a function of the out gassing temperature has been plotted in Figure 3. In which two foremost stepladders of crystallinity forfeiture are perceived, in first one proceeds abode between 200 and 300°C, and the second one fraction from 300 to 400°C, the loss of crystallinity in the concluding step

actuality added vital than in the prior. These two steps correspond closely to the temperature ranges where the decomposition of the organic material takes place, as determined by IR spectroscopy. Moreover, the reduction in the expanse of the key peak after warming at 500°C is further noticeable for nanozeolites with truncated aluminum gratified. In synthesized zeolites also influences their X-ray powder diffraction pattern due to aluminum content. The altitude of the base peak in the patterns diminutions with decreasing Si/Al ratio in the zeolite, but their width increases simultaneously so that the area remains basically constant for all illustrations. Moreover, hkl distance corresponding to the diffraction peak at 43° of 2θ correlated linearly with the aluminum content of the nanozeolite (Figure 4). Further, the nonexistence of acquaintance of the crystal structure of Nanozeolite makes it awkward to draw a parallel the Al content and unit cell parameters.

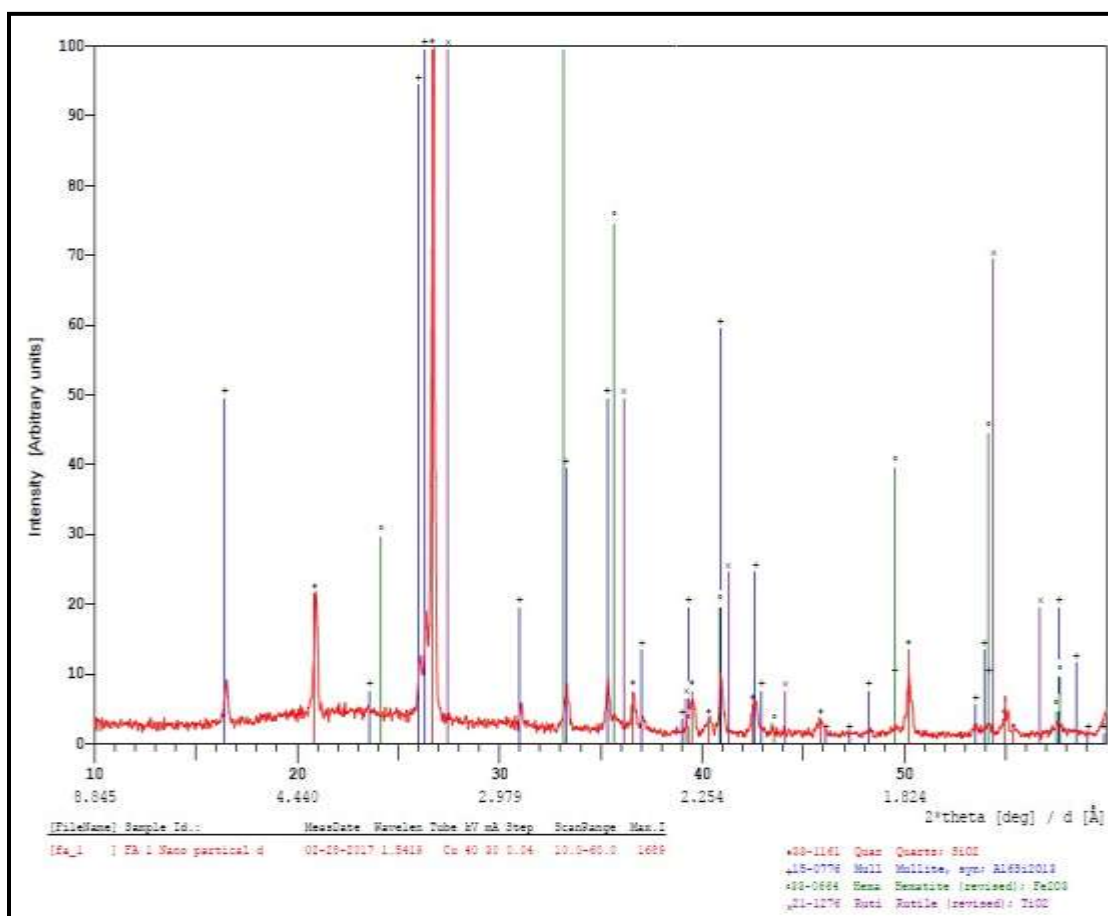


Figure 9: Standard XRD patterns of Nanozeolite

3.3 Scanning Electron Microscopy (SEM):

The nano-zeolite scanned through SEM to know the surface morphology of nano-zeolite before load-ing of nutrients. It showed that the nano-zeolite was typical cubic to round in shape. Surface morphology of nanozeolite after attaching Alumina, which showed there was slight change from original structure. After attachment of Silica oxide there was a substantial reduction in surface area reported that zeolite, which is known as the best absorbent material for metals has the highest cation exchange capacity and shows high adsorption rates.

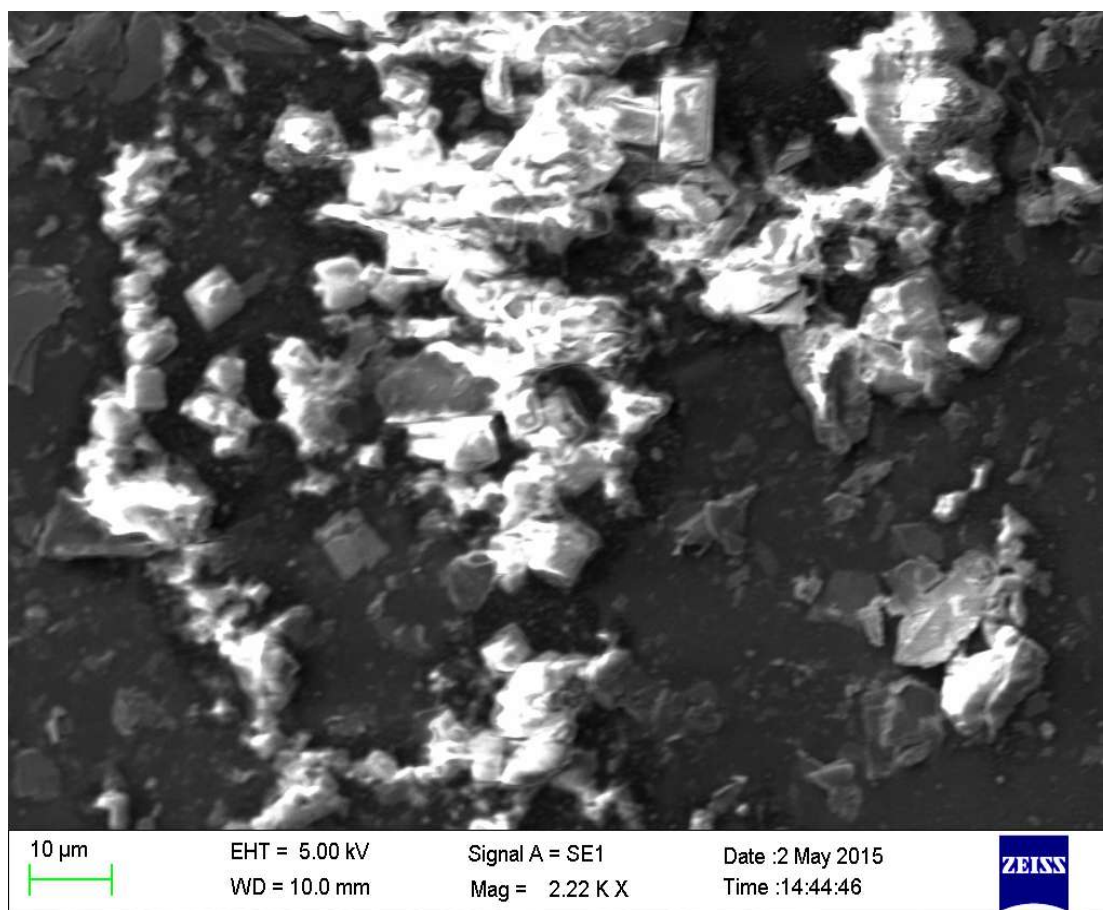


Figure 10: Standard SEM morphology of Nanozeolite

3.4 Acidity

To estimate the acidic nature of the hydroxyl groups or molecule in terms of Lewis acid theory their evolution as a function of its aluminum content. In pyridine adsorption on samples of Beta zeolite with Si or Al ratio between 7 and 40 allow us towards lewis acidity.

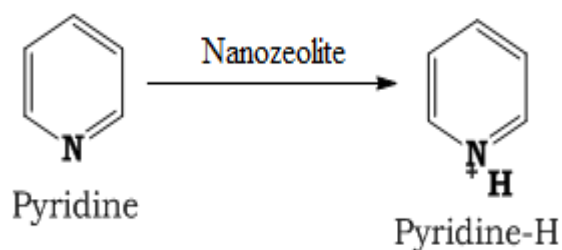


Figure 11: Acidity of Nanozeolite

Conclusion:

The reaction times and yields with PPA, H₂SO₄, and Sulphamic acid were compared with green cyclizing reagent, it was found Nanozeolite is the best recyclable catalyst for this reaction producing excellent yields in reasonable time. Moreover, processes involving the conventional acids are inherently associated with problems such as high toxicity, corrosion, catalyst waste, difficulty in separation and recovery.

Furthermore, through the liquid phase catalyst could be easily separated from the products, it is very difficult to separate them from by-products formed during the reaction. Replacement of these conventional acids by SA is desirable to achieve effective catalysts handling, product purification and to decrease waste production. It was found that with strong heating in muffle furnace at 800⁰C could be recycled without loss any activity.



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