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Bulletin of Chemical Reaction Engineering & Catalysis, 12 (1), 2017, 32-40

Research Article

Modification, Characterization, and Catalytic Application of Mesolite for One Pot Synthesis of 3-Methyl-4-arylmethylene-isoxazol-5(4H)-ones

Ganesh T. Pawar, Sachin P. Gadekar, Balasaheb R. Arbad, Machhindra K. Lande*

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University,
Aurangabad (M.S.), 431004, India

Received: 25th August 2016; Revised: 10th October 2016; Accepted: 17th October 2016

Abstract

Natural mesolite type zeolite was collected, modified by sulphuric acid treatment and characterized by using Powder-X ray diffraction, Scanning electron microscopy and Energy dispersive spectroscopy, Fourier transform infrared spectroscopy. Temperature programmed ammonia desorption, Brunauer-Emmer-Teller surface area analysis. Modified dealuminated mesolite shows an efficient catalytic activity for one pot synthesis of 3-methyl-4-arylmethylene-isoxazol-5(4H)-ones derivatives, via one pot three component condensation of benzaldehyde, ethylacetoacetate and hydroxylamine hydrochloride. Present method offers several advantages over the reported methods like a simple and inexpensive modification of catalyst, mild reaction condition, easy separation of catalyst, simple work-up procedure, non-chromatographic isolation and purification desired product and excellent yield. Furthermore, catalyst could be reused without significant loose in activity. Copyright © 2017 BCREC GROUP. All rights reserved

Keywords: 3-methyl-4-arylmethylene-isoxazol-5(4H)-ones; benzaldehyde; ethylacetoacetate; hyroxylaminehydrochloride; modification of mesolite; natural zeolite

How to Cite: Pawar, G.T., Gadekar, S.P., Arbad, B.R., Lande, M.K. (2017). Modification, Characterization, and Catalytic Application of Mesolite for One Pot Synthesis of 3-methyl-4-arylmethylene-isoxazol-5(4H)-ones. *Bulletin of Chemical Reaction Engineering & Catalysis*, 12 (1): 32-40 (doi:10.9767/bcrec.12.1.655.32-40)

Permalink/DOI: http://dx.doi.org/10.9767/bcrec.12.1.655.32-40

1. Introduction

Nowadays, the development of green protocol for one pot synthesis of heterocyclic organic compound has gain much more attention in green chemistry. Most of the organic condensation, alkylation, acylation reaction are carried out using mineral acid/base and stoichiometric amount of Lewis acids like $AlCl_3$, BF_3, $ZnCl_2$ [1]. Despite its high selectivity, these homogenous classical acid catalysts are inheriting disadvantages like high toxicity, corrosive nature and generation of maximum waste, tedious recovery. Therefore, it is necessary to find sustainable alternatives to these hazardous catalysts by inexpensive, non toxic, reusable solid heterogonous catalyst. Accordingly, number heterogeneous solid acids such as nano mixed metal oxides supported clays, transition metal oxide doped mesoporous silica, zeolites are playing important role in organic synthesis in order to develop cleaner and eco friendly green process [2].

Zeolites are microporous, hydrated aluminosilicates minerals found naturally in the

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* Corresponding Author.
E-mail: mkl_chem@yahoo.com
Telp.: +91 0240 2403311, Fax.: +91 0240 2403335

earth crust, containing polymeric three dimensional networks of $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedron as primary building units. These unites are linked to each other by sharing oxygen atom, they also possesses channels and pore ranging in diameter 3-8 Å and possess Lewis and Brönsted acidity in his framework [3]. Zeolites are obtained either from natural deposits or synthesized. Over 150 type of framework of synthetic zeolites have been reported and six different natural mineral of zeolite have been found in nature with substantial quantity and purity [4]. Natural zeolites are used as water softener, cation exchanger, adsorbent for heavy metal cations and dye molecules [5]. Natural zeolites are the good sensors for ammonia and carbon dioxide molecule [6]. Industrially natural zeolites are used as heterogeneous catalyst for alkylation, acylation, isomerization and petrochemical refining [7-10].

Mesolite is microporous fibrous natrolite type natural zeolite. General molecular formula of mesolite is $[Si_{72}Al_{48}O_{240}]$ and NAT framework topology [11]. There are several modification methods to improve the acidity of zeolites such as hydrothermal treatment, acid/base leaching, H_2O_2 and microwave irradiation etc., among them dealumination of zeolite is useful tool to generate strong Lewis as well as Brönsted acidic sites in zeolite framework which can be achieved by acid treatment. The selective extraction of aluminium leads to formation of silianol nests and mesoporsity [12] in his framework (Scheme-1).

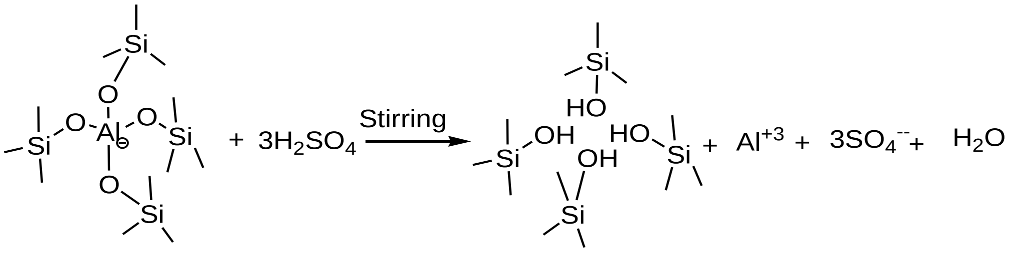
In recent years, isoxazoles derivates have received strong research interest because of their potent biological and pharmaceutical activity such antibacterial, antifungal, anticancer, anti-inflammatory activity [13-15]. Isoxaole derivatives are the building blocks of some natural products [16]. Besides these isoxaole motifs are important constituents of merocyanine dyes [17] and organic optical material [18]. Furthermore, isoxaole derivatives act as fluorescent chemosensor for fluoride aninon [19]. Hence by considering importance and applications of isoxaole derivatives several catalytic methods have been developed using homogenous and heterogeneous catalyst like potassium phthalimide [20], n-bromosuccinimide [21], sodium oxalate, tetra-butylammonium perchlorate, glycine [22], Tartaric acid [23], boric acid [24], DABCO [25], sodium benzoate [26], nano-Fe_2O_3 [27], and $H_3PW_{11}CuO_{40}$ [28]. However, some of them suffered from some problems like harsh reaction condition, long reaction time, low yield and tedious work up for separation of catalyst which generate acidic effluent. Some methods required special conditions such as visible light [29] microwave [30] irradiations and refluxing reaction mixture in toxic homogenous Nitrogen containing organic bases like pyridine [31]. Hence in order to overcome these limitations it is necessary to develop simple, efficient and eco-friendly method for synthesis of 3-methyl-4-arylmethylene-isoxazol-5(4H)-ones derivatives.

In continuation of our research work, on development of heterogeneous catalysts and their utilization for synthesis of heterocyclic organic compounds [32-33]. The present communication report collection, modification and catalytic application mesolite type zeolite sample which was collected from Aurangabad district of Marathwada region, Maharashtra state, India. It was modified by sulphuric acid treatment and characterized by X-ray diffraction, FT-IR, NH_3-TPD, FT-IR, SEM-EDS, and BET and used as heterogeneous solid acid catalyst for one pot synthesis of 3-methyl-4-arylmethylene-isoxazol-5(4H)-ones derivatives, (Scheme-2).

2. Materials and Method

2.1. Chemicals and instruments

All solvents and chemicals were analytical grade and purchased from Merck, Avra and Spectrochem chemicals and used as such. Melting points were taken in an open capillary and are uncorrected. FT-IR spectrum was recorded



Scheme 1. Modification of mesolite by sulphuric acid treatment

on Perkin Elmer; thin layer chromatography was performed on Merck pre-coated silica plates. ^{1}H NMR spectra were recorded on 400 MHz Bruker avance FT-NMR spectrometer in $CDCl_3$ as solvent and chemical shifts values are recorded δ (ppm) relative to tetramethylsilane (Me_4Si) as an internal standard. The X-ray diffraction patterns were recorded on Bruker 8-D advance X-ray diffractometer using monochromatic Cu-Kα radiation (λ = 1.5405 Å). Scanning electron microscope image with energy dispersive X-ray spectroscopy was obtained on JSM - 6390LV6330 LA operated at 30.0 kV. The surface area was calculated by N_2 adsorption performed on Quantachrome CHEMBET 3000 instrument. Temperature programmed ammonia desorption was recorded on micromeritice instrument from room temperature to 700 °C with heating rate 10 °C/min.

2.2. Modification of natural mesolite type zeolite

Natural mesolite powder was washed and refluxed with distilled water for 3 h and dried in an oven at 150 °C for 4 h. The 5 g dried sample was mixed with 20 mL of 0.1 N H_2SO_4. The resulting mixture was stirred continuously for 3 h and filtered by sintered glass crucible the product so obtained was washed with distilled water and dried in an oven at 110 °C for overnight. Finally, the resulting material was calcined in a muffle furnace (SONAR) at 500 °C for 5 h under air atmosphere. The sample were naturally cooled and further named as dealuminated mesolite.

2.3. Typical reaction procedure for the synthesis of 3-methyl-4-arylmethylene-isoxazol-5 (4H)-ones derivatives

A mixture of aromatic aldehyde (1 mmol), hydroxylamine hydrochloride (1 mmol), ethylacetoacetate (1 mmol), and catalytic amount dealuminated mesolite (0.1 g) was stirred in 20 ml of aqueous ethanol (EtOH:H_2O of 3:1) solvent system for the time shown in Table 3. The progress of the reaction was monitored by TLC (petroleum ether : ethyl acetate 7:3 as eluent). After completion of the reaction, the reaction solid crude product was dissolved in hot ethanol and filtered to recover catalyst the filtrate was concentrated under reduced pressure, and the crude product obtained was recrystallized from ethanol to afford pure product.

2.4. Spectroscopic data a representative sample

The spectroscopy data of the 4-(4-methoxybenzylidene)-3-methylisoxazol-5-(4H)-one (3b) yellow solid showed IR (KBr) 3449.25, 3090.80, 2979.37, 1730.73, 1589.49, 1552.20, 1425.08, 1265.23 cm^{-1}, ^{1}H NMR 2.279, (s 3H, CH_3), 3.918 (s, 3H, OCH_3) 7.00-7.023 (d, 2H), 7.341 (s, 1H), 8.428-8.451 7.6 (d, 2H).

3. Results and Discussion

3.1. X-ray diffraction (XRD)

XRD patters of parent and dealuminated mesolite are given in Figure 1 shows intense peaks at 2θ° = 13.57, 19.35, 20.39, 24.599, 27.81, 31.14, 34.87, 39.84 with corresponding planes (0 1 1), (4 1 0), (3 3 1), (5 3 0), (5 1 1), (1 9 2), (3 21 0), (2 17 2), respectively, which are characteristic peaks of mesolite type natural zeolites [34]. The diffraction planes of dealumi-

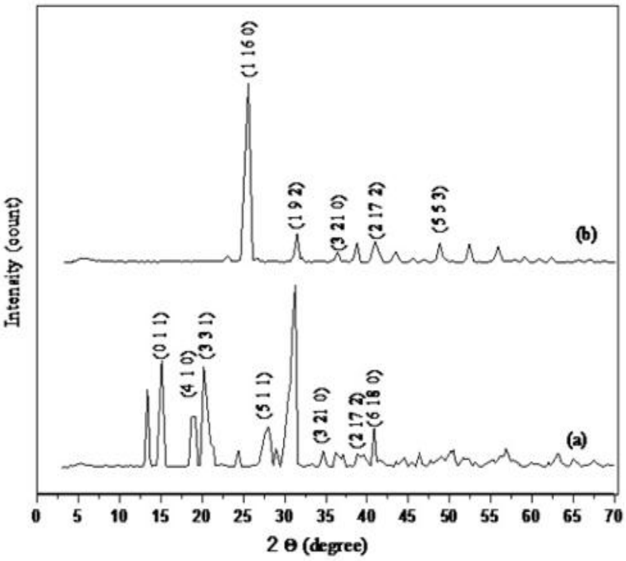
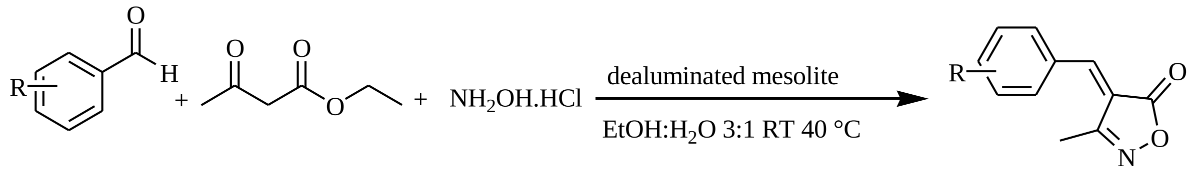


Figure 1. Powder XRD pattern of (a) parent natural mesolite (b) dealuminated mesolite



Scheme 2. Synthesis of 3-methyl-4-arylmethylene-isoxazol-5(4H)-ones derivatives

nated mesolite shows low intensity due to loss of crytallinity and leaching of aluminum from framework, but both the samples are in orthorhombic phase.

3.2. Scanning electron microscopy-energy dispersive spectrometry (SEM-EDS)

Scanning electron microscopy and Energy Dispersive Spectroscopy has been extensively used to study surface morphology and elemental composition of catalytic material. The SEM image of parent and dealuminated mesolite is presented in Figures 2(a) and (b) shows rod shaped crystals. The SEM image of sample (b) shows small but less bulky crystals, this may be due to generation of mesoporsity because of acid leaching. The elemental composition of mesolite is shown in Figure 3 which show the presence of O, Al, Si, Ca, elements, with (atom %) 38.47, 20.36, 28.19, 12.2, respectively. From EDS spectrum we have calculated empirical formula for parent mesolite is $Si_3Al_2Ca_1O_4$. The Figure 3(b) present EDS profile of dealuminated mesolite having elemental distribution in (atom %) O, Al, Si of 38.47, 2.34, 59.19 % respectively, with corresponding empirical formula $Si_{30}AlO_{19}$. It has been found that Si:Al ratio increases on acid treatment.

3.3. Fourier transform infrared spectroscopy (FT-IR)

FT-IR Spectroscopy is used to study the framework and structural building unites of zeolites. Figure 4 (a-c) shows the FT-IR spectra

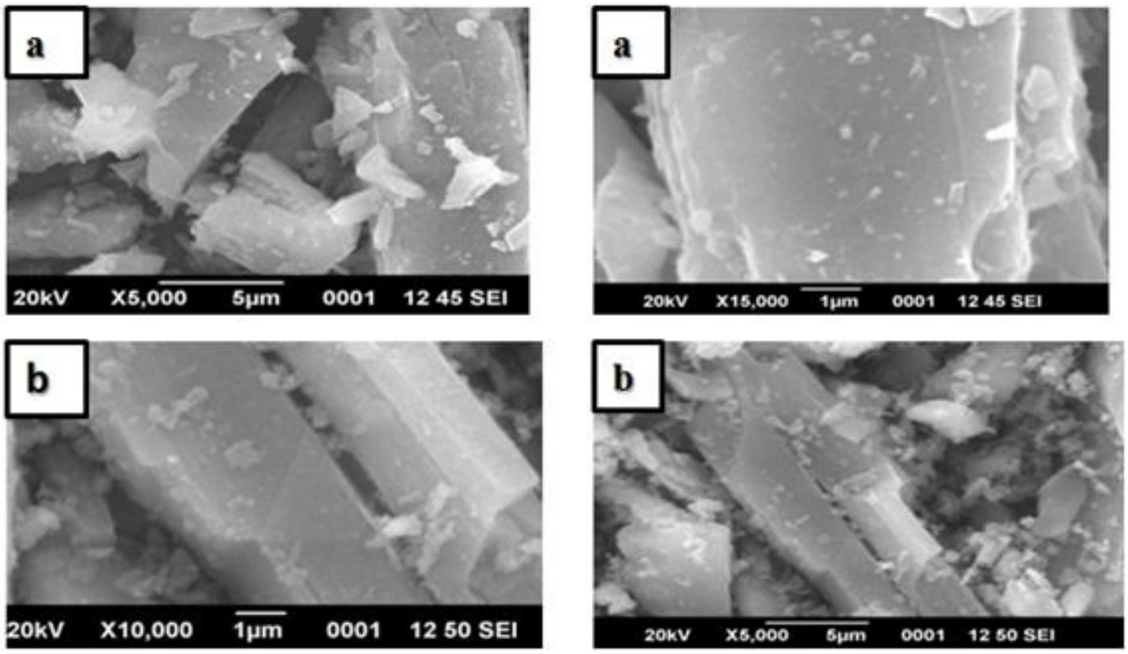


Figure 2. SEM-images of (a) parent natural Mesolite (b) dealuminated Mesolite.

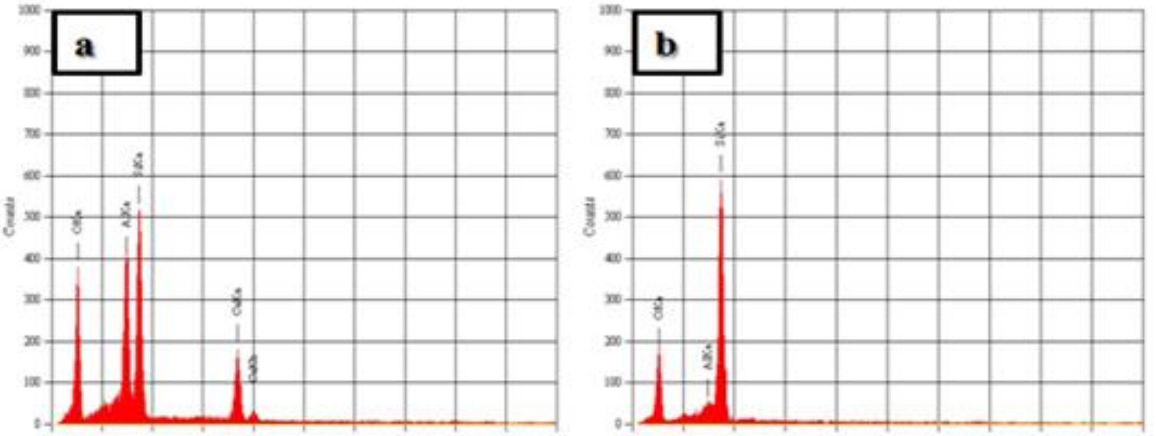


Figure 3. EDS-Spectrum of (a) parent mesolite (b) dealuminated mesolite

of the mesolite. Figure 4(a) shows peak at 3756 cm^{-1} is due to the Si–OH stretching vibration, 1689 cm^{-1} for the Si–OH bending mode, and 965 cm^{-1} due to the Si–O–Si or Al–O–Si stretching vibration mode [35]. Figures 4(b) and 4(c) shows disappearance of band at 965 cm^{-1} this may be due to breaking of Si–O–Si or Al–O–Si framework and shows broad band between 3479-3756 cm^{-1} confirms presence of surface hydroxyl group [36].

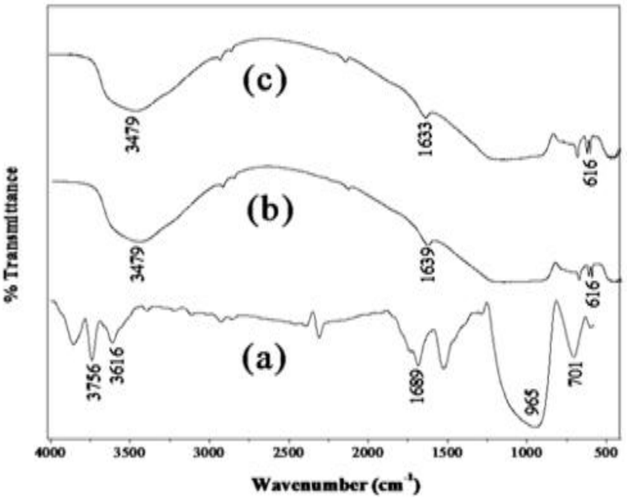


Figure 4. FT-IR spectrum of (a) parent mesolite, (b) calcined mesolite, (c) dealuminated mesolite.

3.4. Temperature programmed ammonia desorption (NH_3-TPD)

The Figure 5(a) and (b) shows NH_3-TPD profile of parent and acid treated (dealuminated) mesolite. The Figure 5(a) shows two distinct peaks in the range 150-500 °C due to the presence of different types of acidic sites in the framework. The desorption peak observed at 196.2 °C is due to presence of bridged hydroxyl group or Brönsted acidic sites. While peak observed at 420.9 °C is due desorption of NH_3 from strong Lewis acidic sites. Figure 5(b) shows single peak at 308.9 °C is due to desorption of ammonia from Brönsted acidic sites [37]. From Table 1, the total acidity of parent mesolite and dealuminated mesolite is found 0.3724 and 0.5726 mmol.g^{-1} respectively. Therefore, acid treated mesolite shows more acidity than parent mesolite this may be due to increase in Lewis acidic sites because of dealumination. Surface area and porosity of catalyst were measured by Nitrogen adsorption desorption method. The BET surface area of dealuminated mesolite is found 4.486 m^2/g which is greater than parent mesolite.

3.5. Catalytic activity result

In order to investigate optimum loading of catalyst and suitable solvent medium for present protocol 4-OCH_3 benzaldehyde (1 mmol) were reacted with ethylacetoacetate (1 mmol)

Table 1. Acid strength and BET surface area of mesolite

Sr. No.	Catalyst	Total acidity mmol.g^{-1}	BET surface area m^2/g
1	Parent mesolite	0.3724	0.1485
2	Dealuminated mesolite	0.5726	4.4863

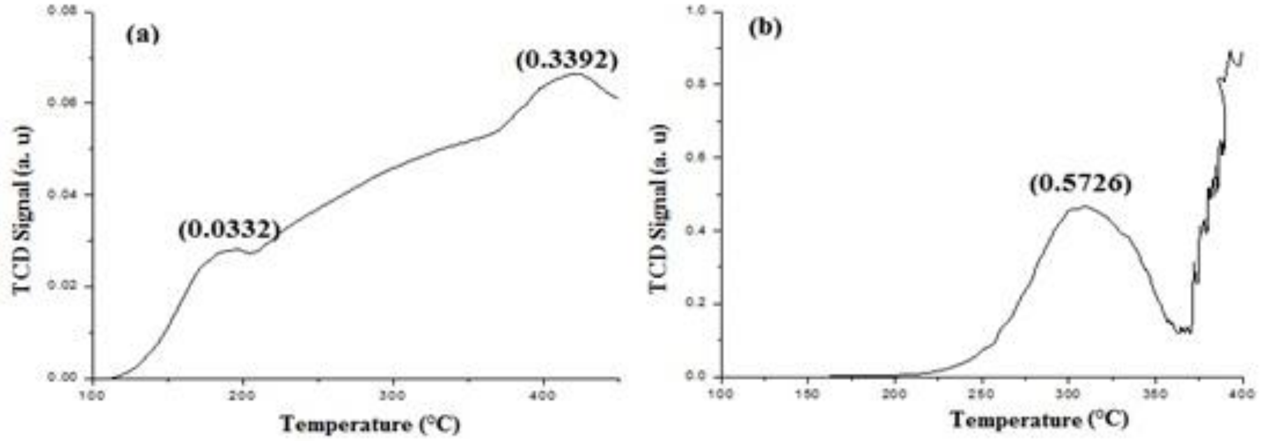


Figure 5. (a) NH_3-TPD of parent mesolite (b) NH_3-TPD of dealuminated mesolite

and hydroxylamine hydrochloride (1 mmol) as model reaction with different solvents and amount of dealuminated mesolite as catalyst at ambient condition (stirring) condition and results are summarized in (Table 2). In the absence of catalyst the reaction did not gave satisfactory yield of desired product (3b), which indicate important role of catalyst, 0.1 gm of dealuminated mesolite is suitable to catalyze reaction smoothly. The same reaction was carried out under optimum loading of catalyst under different solvents, and it is observed that the no single solvent gave excellent yield of desired product, hence we have used mixture of EtOH and H_2O (1:1) as solvent for reaction, surprisingly reaction proceeds faster and maximum yield than other solvent system.

In order to explore the scope and importance of the present method different aromatic aldehydes were tested under optimum reaction conditions for synthesis of 3-methyl-4-arylmethylene-isoxazol-5(4H)-ones derivatives (Table 3). The aldehydes with electron donating groups at para position such as 4-OCH_3, 4-CH_3, 4-OH, were react fast and give maximum yield in minimum time as compare to aldehydes having electron withdrawing group such as, 4-Cl which give tracer yield. After optimizing reaction conditions, efforts have been made towards the recovery and reusability of the catalyst. After completion of reaction solid product was dissolved in hot ethanol and filtered. The recovered catalyst was washed with acetone and activated by drying at 150 °C for 3 hour before the next catalytic run. The reusability of the catalyst was investigated for two times and it was found to retain almost consistent activity (Table 3, entry 3b).

To specify the advantages of proposed method, results of different reported methods

Table 2. Optimization of catalyst loading with different solvents for the synthesis of 3a

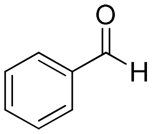
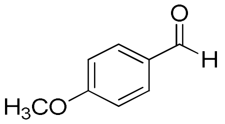
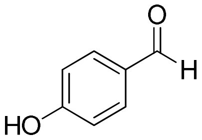
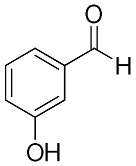
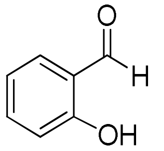
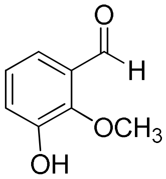
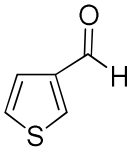
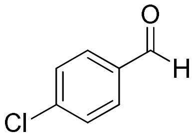
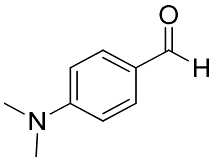
Entry	Solvent	Catalyst amount (g)	Time (min)	Yield(%)[a]
1	Ethanol	-	120	33
2	Methanol	-	120	30
3	Acetonitrile	-	120	28
4	1,4-dioxane	-	120	27
5	Tetrahydrofuran	-	120	25
6	Water	-	120	53
7	Ethanol	0.05	60	65
8	Ethanol	0.1	60	67
9	Ethanol	0.15	60	67
10	Ethanol	0.2	60	68
11	Ethanol:Water (3:1)	0.1	60	95
12	Ethanol:Water (1:3)	0.1	60	85
13	Ethanol:Water (1:1)	0.1	60	89

[a]isolated yield

Table 4. Catalytic performance of different catalysts for the synthesis of 3-Methyl-4-arylmethylene-isoxazol-5(4H)-ones derivatives

Entry	Catalyst	Condition	Time (min)	Yield (%)	References
1	Pottasium phthalimide	Water, R.T.	70	96	(20)
2	N-bromosuccinimide	Water, R.T.	100	88	(21)
3	Sodium oxalate	Water, R. T.	70	90	(22)
4	Tartaric acid	Water R.T.	35	93	(23)
5	Sodium tetraborate	Water R.T.	50	90	(24)
6	Pyridine	reflux in ethanol	60	93	(31)
7	Dealuminated mesolite	Starring in ethanol : water (3:1)	60	95	Our results

Table 3. Dealuminated mesolite catalyzed cyclocondensation of aromatic aldehyde, elthylacetoacetate and hydroxylamine hydrochloride.

Entry	Aldehyde (R)	Time (min)	Yield (%)[a]	M.P. (°C)	
				Observed	Literature
3a.		110	90	140	140-142[21]
3b.		60	95(93,92,)[c]	174	175-177[21]
3c.		60	93	211	210-211[21]
3d.		120	85	198	199-201[20]
3e.		130	80	190	189-2021[20]
3f		120	88	212	213-215[20]
3g		120	85	145	145-147[29]
3h		120	Trace	------	-----
3i		100	90	220	220-221[21]

Reaction conditions: benzaldehyde (1 mmol), ethylacetoacetate (1 mmol), hydroxyl aminehydrochloride (1 mmol), catalyst 0.1 g, and ethanol : water (1:1) 15 mL. [a]Isolated yields. [c]Yield after consecutive cycle are compared with our results and are summarized in Table 4. It is found from tabulated results that, dealuminated mesolite promotes reaction more effectively under mild condition than other reported methods. Furthermore reported methods require additional workup to recover and reuse catalyst.

4. Conclusions

In summary, we have successfully modified natural mesolite zeolite by heat and H_2SO_4 treatments. Present modification method is simple and inexpensive. XRD and SEM-EDS analysis confirms the mesolite phase of natural zeolite. FT-IR, analysis identifies bridged and surface hydroxyl groups present in a zeolite. NH_3-TPD analysis confirms presence of both weak and strong acidic sites in a natural zeolite. It has been found that the active sites and surface area was increased by H_2SO_4 treatment as compared to parent natural zeolite. The modified dealuminated mesolite is used as heterogeneous catalyst for the synthesis of 3-methylarylmethylene-isoxazol-5(4H)-ones derivatives by condensation reaction between aldehyde, ethylacetoacetate and hydroxyl amine hydrochloride. Present method offers remarkable advantages such as non-toxic, non-corrosive and an inexpensive reaction conditions. Simple recovery and reusability of the catalyst make the reaction successful under environmental benign conditions.

Acknowledgement

We are grateful to the Head, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad–431004 (MS), India for providing the laboratory facility. The authors are thankful to STIC Cochin and IIT Madras for providing characterization facilities.

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