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Fe-MCM-22 catalyzed multicomponent synthesis of dihydropyrano [2,3-c] pyrazole derivatives

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ABSTRACT

The Fe-MCM-22 zeolite was found to be an efficient solid heterogeneous catalyst for synthesis of dihydropyrano [2,3-c] pyrazoles via one pot four component reaction of ethyl acetoacetate, hydrazine hydrate, aromatic aldehyde and malononitrile in aqueous alcohol. The catalyst was synthesized by hydrothermal method under autogenous pressure and modified by Fe (III) ion exchange. The prepared catalyst was characterized by X-ray diffraction (XRD), Scanning Electron Microscopy-Energy Dispersive spectroscopy (SEM-EDS), Fourier Transform Infrared Spectroscopy (FT-IR), and Brunauer-Emmett-Teller (BET) measurement technique. This ecofriendly protocol provides several advantages such as use of an inexpensive catalyst, short reaction time, mild reaction condition, simple work-up, good to excellent yield and reusability of the catalyst.

Keywords: *Fe-MCM-22 zeolite, Multicomponent synthesis, Heterogeneous catalyst, Dihydropyrano [2,3-c] pyrazoles.*

1. Introduction

The significant challenge in the synthetic chemistry is to develop environmentally benign, efficient and economical methods for the synthesis of biologically active compounds [1]. Multi-component reactions (MCRs) have become one of the best tools for modern synthesis of chemically and biologically important compounds because of their high atom economy, simple procedure and excellent yields [2-4]. The synthetic utility of such protocols is further made more effective when the reactions are carried out in the presence of reusable heterogeneous catalyst. Recently, for the sustainable development of any catalytic process, heterogeneous catalyst have been used because of their easy recovery, recyclability, minimization of undesired toxic wastes, and E factor [5].

Pyrano [2,3-c] pyrazole derivatives have attracted the attention of researcher because of their potential applications as active pharmaceutical ingredients and biodegradable agrochemicals [6-10]. They also exhibit antimicrobial [11], anticancer [12], anti-inflammatory [13], analgesic [14], insecticidal [15], molluscicidal [16] and human Chk1 kinase inhibitory activity [17].

Literature survey revealed that there are several methods that have been reported for the synthesis of pyrano [2,3-c] pyrazole derivatives employing, piperazine [18], piperidine [19], N-methylmorpholine [20], per-6-amino-β-cyclodextrin [21], glycine [22] L-proline [23], alumina [24], CTACl [25], amberlyst A21 [26], ANL [27], Meglumine[28], [Hmim][HSO_4] [29] and ChCl/Urea DES [30] as catalyst. Although these methods are quite effective, some of them suffer from several drawbacks such as use of volatile and hazardous solvent, high temperature, long reaction time, low yields, tedious work-up procedure and use of expensive and toxic catalyst which also lack reusability. Thus, the development of efficient and environmentally benign protocol for the synthesis of these heterocycles is highly desirable.

Zeolites are microporous, crystalline, aluminosilicate compounds composed of staggered framework of $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedral which are linked by sharing oxygen atom. In framework each aluminum tetrahedron contributing a single negative charge which is balanced by counter metal cataions such as Na, K, Mg, Ca etc. Zeolites have extensive applications in the field of heterogeneous catalysis due to their tunable larger pore sizes and inherent acid/base catalytic properties and provide greener alternatives to homogeneous catalysis [31]. MCM-22 zeolite [32] has been found to be efficient solid acid catalyst because it

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possesses Lewis/ Bronsted acidic sites, high surface area and well defined porosity. The MCM-22 zeolite shows a good catalytic activity and is used for several industrial processes such as alkylation, aromatization, disproportionation of toluene and catalytic cracking [33-36]. In order to modify surface and catalytic properties of MCM-22 various transition and other metals are doped in the extra-framework position [37].

Thus, in continuation to our research work [38], herein we report an environmentally benign and efficient protocol for four-component synthesis of dihydropyrano [2,3-c] pyrazole derivatives in aqueous ethanol at 60°C in the presence of Fe-MCM-22 zeolite catalyst (Scheme 1).

2. Experimental

2.1. Chemicals and Instruments

All the chemicals were purchased from Merck, Avra and Spectrochem and were used without purification. Thin layer chromatography was performed on Merck pre-coated silica gel $60F_{254}$ aluminum sheets as adsorbent. Melting points were taken in an open capillary and are uncorrected. FT-IR spectra were recorded on Thermo Nicolet; Avatar 370. ^{1}HNMR spectra were recorded on a 400 MHz using DMSO-d_6 as solvent and tetramethylsilane (TMS) as an internal standard. The X-ray diffraction (XRD) patterns were recorded on Bruker AXS D8Advance X-ray diffractometer using monochromatic Cu-Kα radiation having wavelength $\lambda = 1.5406$ Å. Scanning Electron Microscope image (SEM) was obtained on JSM-6390 LV operated at 30.0 KV. Surface area and porosity (BET) of catalyst was measured on micromeritics, ASAP 2010 instrument.

2.2. Catalyst preparation

MCM-22 zeolite was synthesized under hydrothermal condition. In a typical synthesis of MCM-22, tetraethyl orthosilicate (TEOS 20.8 g) was mixed in 50 mL deionized water under stirring at room temperature for 2 h then $NaAlO_2$ (0.246 g) was dissolved in 20 mL deionized water added drop wise to above solution. The resulting mixture was stirred at room temperature for 2 h. 2 g of cetyltrimethyl ammonium bromide (CTAB) was added as a structure directing agent and NaOH was added to maintain the pH of solution about 12. The resulting mixture was stirred at room temperature for 12 h to complete the hydrolysis of TEOS and $NaAlO_2$. The viscous gel was transferred into Teflon lined stainless steel autoclave. The crystallization of gel was carried out at 150°C for 24 h. The solid product was collected, filtered and washed with deionized water. Finally, it was dried in oven and calcined at 500°C for 5 h in muffle furnace.

For the enhancement of Lewis acidic site in the catalyst, Fe (III) exchanged MCM-22 catalyst was prepared by ion exchange method. In this procedure, 2 g of the MCM-22 and 20 ml of 0.1M Fe $(NO_3)_3.9H_2O$ solution were stirred at 60 °C for 12 h. The resulting product (Fe-MCM-22) was filtered and washed several times with deionized water and dried at 100°C for 4 h.

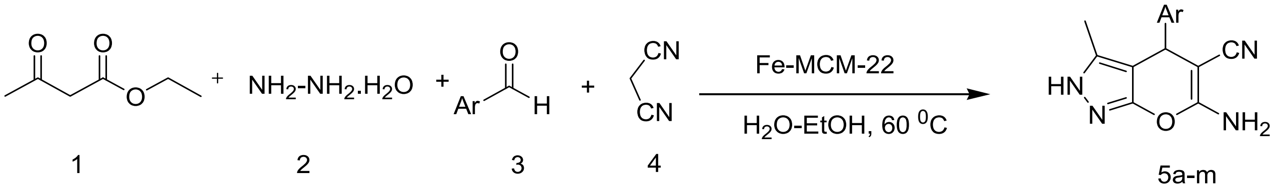
2.3. General procedure for the synthesis dihydropyrano [2,3-c] pyrazole derivatives

To a mixture of ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), aromatic aldehyde (1 mmol), malononitrile (1 mmol) and 0.1 g Fe-MCM-22 catalyst in aqueous ethanol (10 mL) as solvent were added and stirred at 60°C for the time shown in Table 4. The progress of the reaction was monitored by TLC (petroleum ether: ethyl acetate =8:2 as eluent). After completion of the reaction, the reaction mixture was filtered, the catalyst was separated and the crude product obtained was recrystallized from ethanol to afford pure product (5a-m) and characterized by ^{1}HNMR, ^{13}CNMR and mass spectroscopy.

Selected spectral data

*6-Amino-4-(4-bromo-phenyl)-3-methyl-1,4-dihydro pyrano [2,3-c] pyrazole-5-carbonitrile (**5m**):*

White solid. ^{1}HNMR (400 MHz, DMSO-d_6): δ = 1.81 (3H, s), 4.65 (1H, s), 6.86 (2H, s, $-NH_2$), 7.13 (2H, d, $J = 8.1$ Hz), 7.48 (2H, d, $J = 8.4$ Hz), 12.12 (1H, s, –NH) ppm. ^{13}CNMR (100 MHz, DMSO-d_6): δ = 9.7, 35.7, 56.7, 97.3, 119.7, 120.8, 129.6, 131.2, 135.6, 143.6, 154.6, 160.8 ppm. LC-MS [$C_{14}H_{11}BrN_4O$]: m/z = 331.15 (100%).



Scheme1. Synthesis of dihydropyrano [2, 3-c] pyrazole derivatives.

3. Results and Discussion

3.1. Catalyst characterization

The XRD pattern of MCM-22 zeolite and Fe-MCM-22 is depicted in (Fig. 1). The samples show low intense peaks at 2θ = 7.18, 13.16, 14.83, 18.04 and high intense peak at 2θ = 22.26 with corresponding planes (1 0 0), (1 1 1), (2 0 1), (2 0 3) and (1 0 6) respectively, which are characteristic peaks of MCM-22 type zeolites [39]. The broad peak at 20-30 indicates the amorphous nature of prepared MCM-22 type zeolite. It is observed that, the intensity of broad peak at 20-30 decreases, this may be due to insertion of Fe (III) ions inside the mesopores of MCM-22. However, structure of MCM-22 zeolite is retained after ion exchange

Fig. 2 shows the SEM images of synthesized MCM-22 and Fe-MCM-22 zeolite. Fig. 2(a) shows nano flakes associated with mesoporous silica while Fig. 2(b) shows more aglomarization of nano flakes with amorphous silica this may be due to impregnation of Fe (III) inside the amorphous walls of MCM-22 zeolite. The SEM images of synthesized material are similar to those which are reported in literature for MCM-22 type zeolite [40].

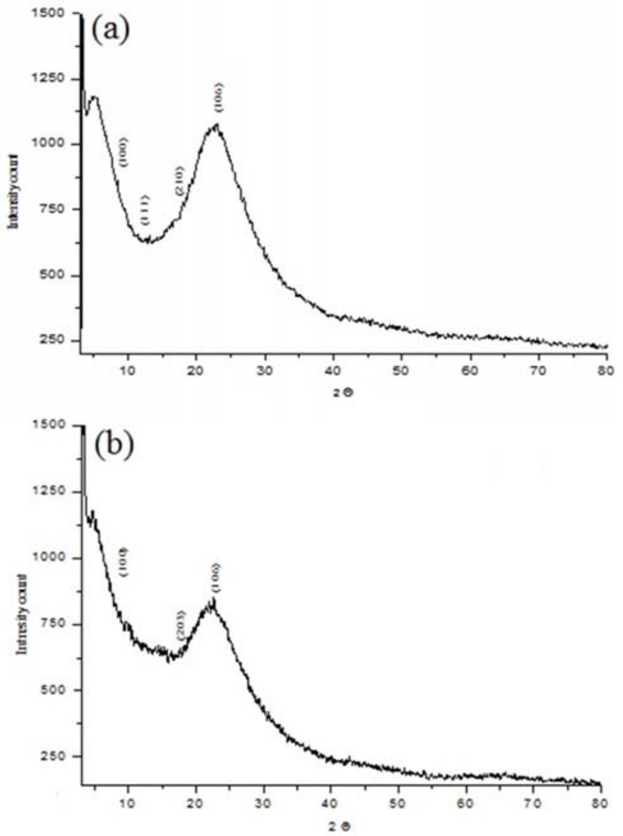


Fig. 1. Powder XRD pattern of (a) MCM-22 Zeolite (b) Fe-MCM-22 Zeolite.

The elemental composition of Fe-MCM-22 is shown in Fig. 2(c) which show the presence of O, Si, Al and Fe elements, with (atom %) 67.81, 30.49, 0.91 and 0.79 respectively. From EDS spectrum, the calculated empirical formula for Fe-MCM-22 was $Si_{39}AlFeO_{86}$.

The FT-IR spectrum of the MCM-22 and Fe-MCM-22 zeolite are shown in (Fig. 3). The FT-IR spectrum shows a sharp peak with high intensity at 1089 cm^{-1} is assigned for asymmetric stretching vibration of T-O-T (T= Si or Al) unit. The sharp band at 459 cm^{-1} is assigned to the T-O bending mode [41]. The sharp band observed at 809 cm^{-1} is due to T-O-T symmetric stretching which has less intensity compared to the asymmetric stretching of T-O-T band. The peak around 1633cm^{-1} is assigned to bending mode of Bronsted acidic site. The introduction of Fe (III) ion into the tetrahedral site of zeolite generates Si-(OH)-Fe Bronsted acid sites, which is observed broad band at 3475 cm^{-1} [42].

Surface area and porosity of catalyst were measured by Nitrogen adsorption desorption method. The BET surface area, micropore volume and average pore diameter for MCM-22 and Fe-MCM-22 are listed in the (Table 1). It was observed that surface area, micropore volume and average pore diameter of Fe-MCM-22 decreased as compared to MCM-22 zeolite which implies that Fe (III) ions are well dispersed in framework.

3.2 Optimization of reaction conditions

In order to optimize the reaction condition, ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), 4-bromo benzaldehyde (1 mmol) and malononitrile (1 mmol) were taken as model substrates. The amount of catalyst was studied in the model reaction at 60°C in EtOH: H_2O (8:2) as solvent. It was observed that 0.1 g of Fe-MCM-22 catalyst was sufficient for completing the reaction. In the absence of catalyst we did not get desired product and use of excessive catalyst had no effect on either the rate of reaction or on the product yield (Table 2).

The reaction medium is the important factor which influences the yield and rate of reaction. In order to examine the solvent effect, the model reaction was carried out in various solvent as shown in Table 3. When the reaction was performed under solvent free condition low yield of product was obtained. Further we used different solvent condition like H_2O, MeOH, EtOH, THF and EtOH: H_2O (8:2). Among all these solvents, the mixture of EtOH and H_2O (8:2) gave excellent yield.

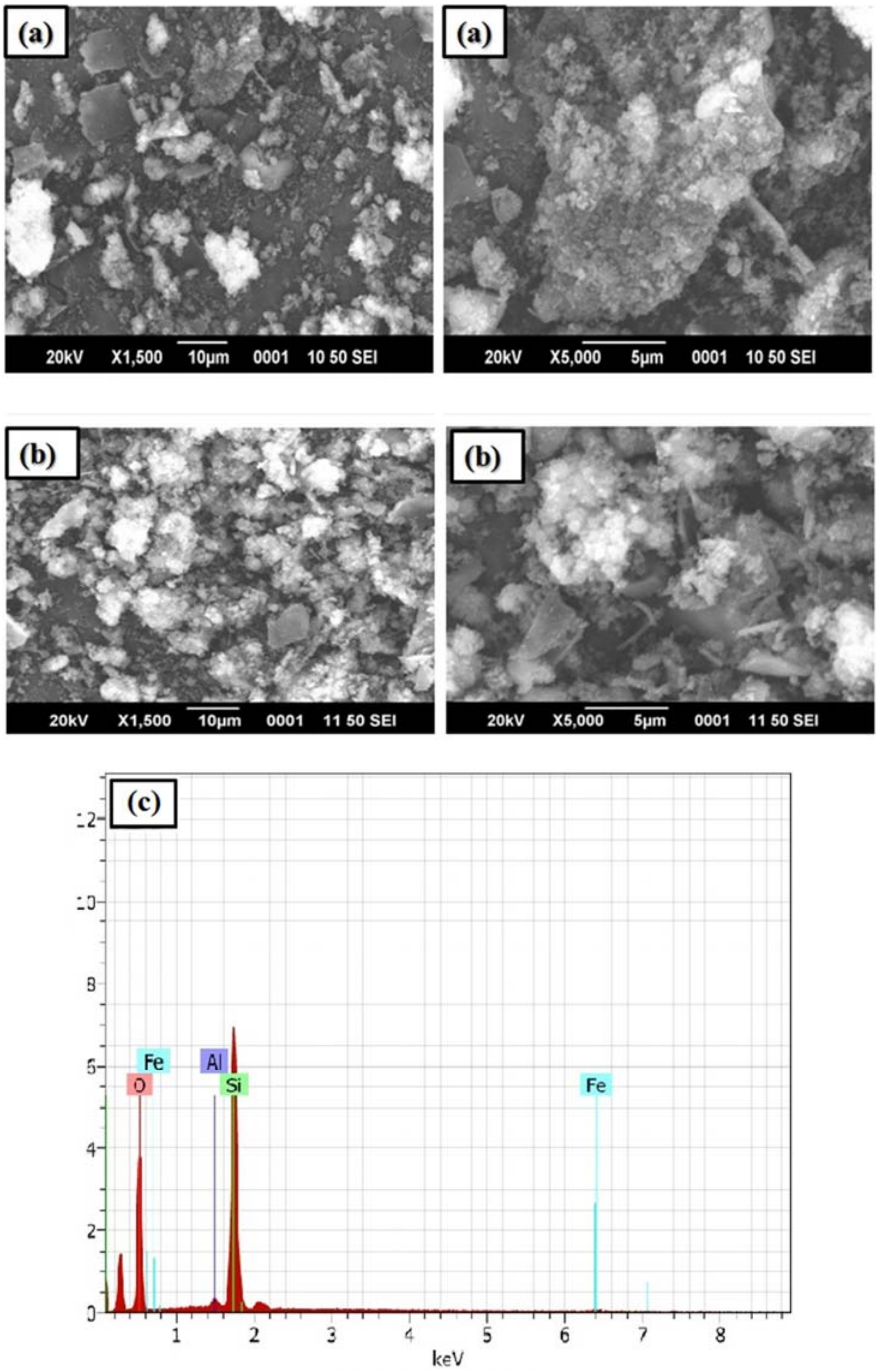


Fig. 2. (a) SEM-images of MCM-22 zeolite (b) SEM-images of Fe-MCM-22 zeolite and (c) EDS Spectrum of Fe-MCM-22 zeolite.

After optimizing the reaction conditions, the scope and efficiency of the present method were studied. A series 6-Amino-3-methyl-4-phenyl-2,4-dihydropyrano [2,3-c] pyrazole-5-carbonitrile was prepared by using various substituted aromatic aldehyde reacting with hydrazine hydrate, ethyl acetoacetate and malononitrile in aqueous ethanol in the presence of Fe-MCM-22 zeolite catalyst (Table 4). It was found high yields of the products were obtained with aldehydes having electron withdrawing groups like 4-Cl, 2-Cl, and 4-NO_2 as compared to aldehydes having electron donating group like 4-OH, 4-OCH_3 in stipulated time.

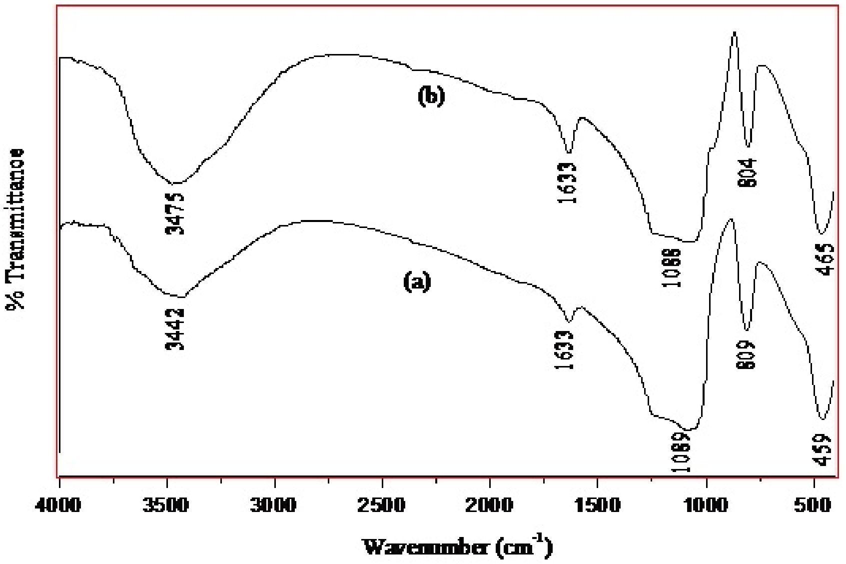


Fig. 3. FT-IR spectrum of (a) MCM-22 zeolite (b) Fe-MCM-22 zeolite.

Table 1. BET surface area, micropore volume and average pore diameter for MCM-22 and Fe-MCM-22.

Sr. No.	Sample	Surface area (m^2/g)	Micropore volume (cm^2/g)	Average pore diameter (Å)
1	MCM-22	601.39	28.05	1866
2	Fe-MCM-22	103.83	0.08	31.29

Table 2. Optimization of catalyst loading.

Entry	Catalyst amount (g)	Time (min)	Yield(%)[a]
1	0	50	-
2	0.05	50	80
3	0.10	50	94
4	0.15	50	92
5	0.20	50	92

[a] Isolated yield.

Table 3. Effect of various solvent on the synthesis of dihydropyrano [2, 3-c] pyrazoles derivatives.[a]

Entry	Solvent	Time (min)	Yield (%)[b]
1	No	80	20
2	H_2O	80	50
3	MeOH	80	70
4	EtOH	80	70
5	THF	80	65
6	EtOH:H_2O	50	94

[a] Reaction conditions: Ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), 4-bromobenzaldehyde (1 mmol), malononitrile (1 mmol), catalyst (0.1 g) and solvent (10 mL).

[b] Isolated yields.

Table 4. Fe-MCM-22 catalyzed synthesis of dihydropyrano [2,3-c] pyrazole derivatives.

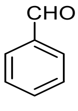
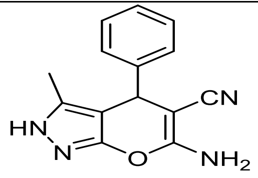
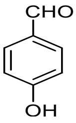
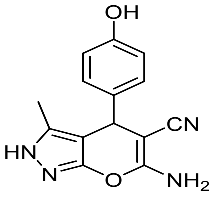
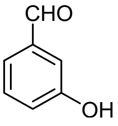
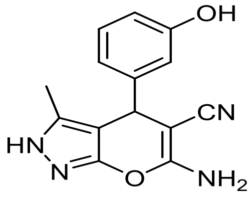
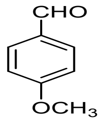
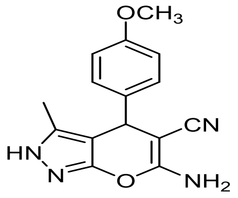
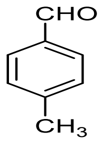
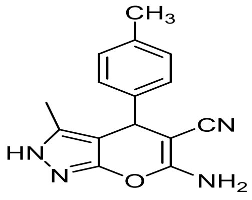
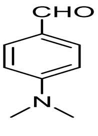
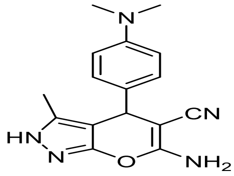
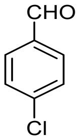
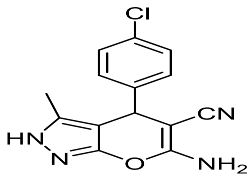
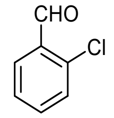
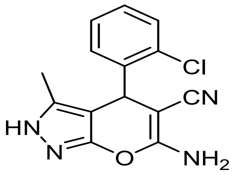
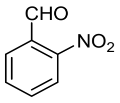
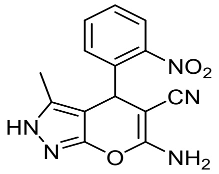
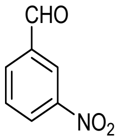
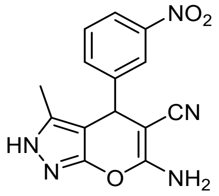
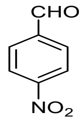
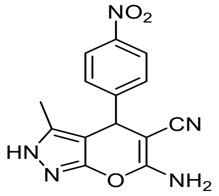
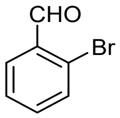
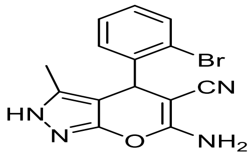
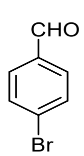
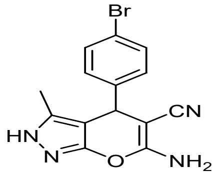
Entry	Aldehyde	Product	Time (min)	Yield (%)	m.p. (°C)		Ref.
					Found	Reported	
1		 **5a**	50	80	243-244	244-245	[27]
2		 **5b**	50	82	224-225	223-224	[28]
3		 **5c**	50	82	219-221	220-222	[27]
4		 **5d**	50	83	210-212	210-212	[28]
5		 **5e**	50	74	203-205	206-208	[24]
6		 **5f**	50	70	166-168	167-169	[24]
7		 **5g**	50	94	232-234	234-235	[28]

Table 4. (*Continued*)

8		 **5h**	50	94	144-146	145-147	[24]
9		 **5i**	50	93	223-225	223-224	[27]
10		 **5j**	50	94	190-192	191-192	[27]
11		 **5k**	50	94	248-250	250-253	[29]
12		 **5l**	50	92	180-185	-	-
13		 **5m**	50	94	178-180	180-181	[29]

[a]Reaction condition: Ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), aromatic aldehyde (1 mmol), malononitrile (1 mmol), catalyst (0.1 g), and aqueous ethanol 10 mL.

[b]Isolated yields.

After optimizing reaction conditions, efforts have been made towards the recovery and reusability of the catalyst. The main advantage of present method is reusability of Fe-MCM-22 zeolite catalyst and efficient recovery. The catalyst was separated after completion of reaction by diluting reaction mixture by hot ethanol and filtration. The recovered catalyst was washed with acetone and dried at 100 °C for 3 h before the next catalytic run. Reusability of the catalyst was investigated on model reaction for three times and it was found that the catalyst had retained almost consistent activity (Table 5).

Table 5. Catalyst reusability.

No. of cycle	Catalyst Recovery (%)	Yield (%)[a]
Fresh	95	94
1st	95	90
2nd	90	85
3rd	85	85

[a]Isolated yield.

To specify the advantages of proposed method, results of different reported methods were compared with present results summarized in (Table 6). It is clear that, Fe-MCM-22 zeolite promotes reaction more effectively than other reported method under mild condition.

The plausible mechanism that could be accounted for the multicomponent synthesis of dihydropyrano [2,3-c] pyrazole is depicted in scheme-2. The Fe-MCM-22 possesses Lewis and Bronsted acidity. In the first step reaction between ethyl acetoacetate and hydrazine hydrate takes place which gives pyrazolones 6. In the second step Knoevenagel condensation between aldehyde and malononitrile takes place to give ylidenemalononitrile 7. In the third step Michael addition of pyrazolone to ylidenemalononitrile takes place which is followed by cyclization and tautomerization to give pyrano pyrazole 5.

4. Conclusion

In summary, we described the synthesis of MCM-22 zeolite catalyst by hydrothermal method and modified by Fe (III) ion exchange. By using this catalyst we developed green and efficient approach for the synthesis of dihydropyrano [2, 3-c] pyrazole derivatives. The advantages of present method are use of inexpensive catalyst, short reaction time, mild reaction condition, simple reaction workup, good to excellent yield and reusability of catalyst.

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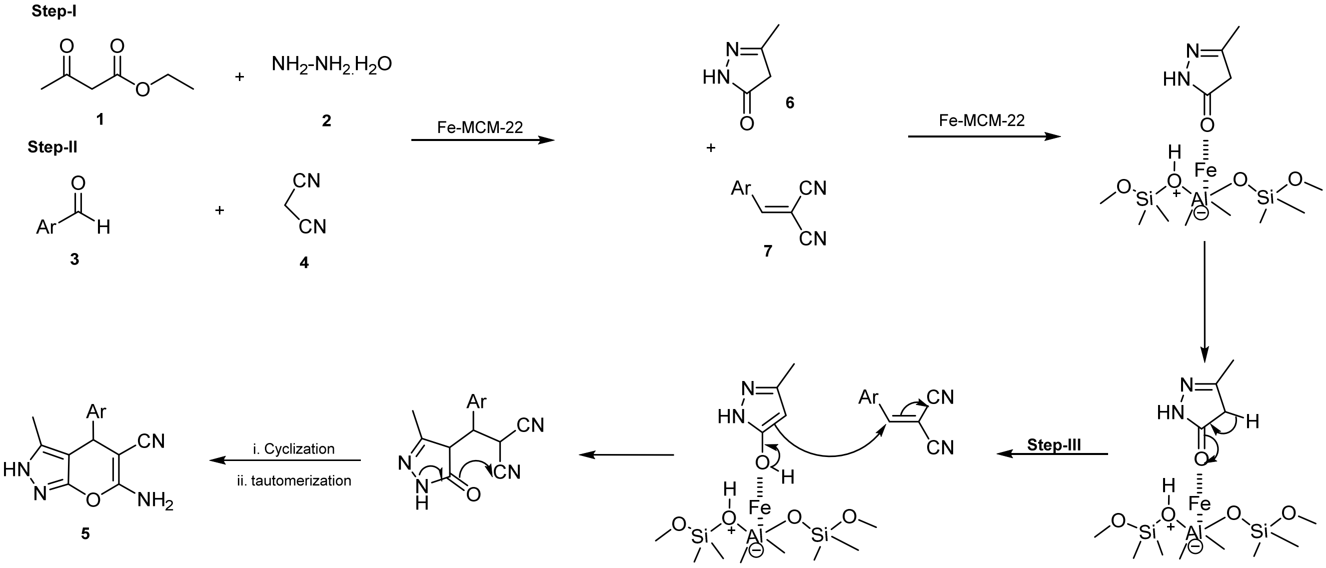
Table 6. Comparison of reported methods for synthesis of dihydropyrano [2, 3-c] pyrazole with Fe-MCM-22 catalyst.

Entry	Catalyst	Solvent/condition	Time (min)	Yield (%)	Ref.
1	Piperidine	water, r.t.	5-10	83	[19]
2	N-methyl morpholine	EtOH, r.t.	15	98	[20]
3	Per-6-amino-β-cyclodextrin	solvent free, mixing r.t.	1	99	[21]
4	γ-Alunina (30 mol%)	H_2O, reflux	45	75	[24]
5	CTACl (20 mol%)	H_2O, 90°C	4h	88	[25]
6	Amberlyst A21	EtOH, r.t.	15	98	[26]
7	Lipase from Aspergillus niger	EtOH, 30°C	1-1.5h	98	[27]
8	Meglumine	EtOH-H_2O, r.t.	15	95	[28]
9	[Hmim][HSO_4] 10 mol%	EtOH(50%), 50°C	25	92	[29]
10	Fe-MCM-22	EtOH:H_2O(8:2), 60°C	50	94	This work



Scheme 2. Plausible Mechanism for the formation of dihydropyrano [2, 3-c] pyrazoles.

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