RESEARCH ARTICLE - CHEMISTRY

S. S. Katkar · B. R. Arbad · M. K. Lande

ZnO-Beta Zeolite Catalyzed Solvent-Free Synthesis of Polyhydroquinoline Derivatives Under Microwave Irradiation

Abstract An efficient and environmentally friendly multi-component synthesis of polyhydroquinolines is described. The reaction was catalyzed by zinc modified beta zeolite and performed using microwave irradiation in solvent-free conditions. This reaction was rapid with high yields and a simple workup. The catalyst could be reused several times without significant loss of activity.

Keywords ZnO-beta zeolite · Multi-component reaction · Heterogeneous catalyst · Microwave irradiation

الخلاصة

تصف هذه الورقة العلمية طريقة تحضير متعددة المكونات فعالة و صديقة للبيئة للبولي
هيدروكوينولينز محفزة بالزيولات المعدل بالزنك في وجود إشعاعات مايكروويف ودون استخدام
مذيبات. ولهذه الطريقة حسنات كثيرة منها: قصر وقت التفاعل والإنتاجية العالية و المعملية
البسيطة.

1 Introduction

Multi-component reactions (MCR) involve two or more synthetic steps that are carried out without isolation of any intermediates. This reduces the reaction time, and saves money, energy, and raw materials [1]. Overall, multi-component reactions are more environmentally friendly than conventional reactions.

In microwave chemistry, microwave radiation is applied to chemical reactions as an alternative to conventional heating. The liquid or solid reagents transform the electromagnetic energy into heat for the reaction. Microwave heating has a number of benefits over conventional heating because the absorption and transmission of energy in a microwave reaction are very different to those in a conventional chemical reaction. Microwave technology has been applied to polymer technology, organic synthesis, waste treatment, drug release and targeting, ceramics, and alkane decomposition [2–10].

1,4-Dihydropyridine (1,4-DHP) and its derivatives have emerged as an important class of drugs for the treatment of cardiovascular diseases [11,12]. Dihydropyridyl-based cardiovascular agents effective in the treatment of hypertension include nifedipine, nicardipine, amlodipine, and other related derivatives [13]. 1,4-DHPs function biologically as vasodilators, bronchodilators, and anti-atherosclerotic, antitumor, geroprotective, hepatoprotective, and antidiabetic agents [14–18].

Heterogeneous catalysis in synthetic organic chemistry makes processes more environmentally and economically feasible. Among the various solid acid catalysts, zeolites have received attention because of their

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suitable acidity, thermal stability, simple work-up, recyclability, and environmental friendliness. Zeolites catalysts are used in the petroleum refining and chemical industries [19,20]. Their properties and performance as catalysts can be adjusted by modification via ion exchange with metal ions, acid treatment, and hydrothermal treatment [21,22]. Zinc-loaded zeolites are suitable for various organic transformations, such as the Heck reaction [23], propane aromatization [24], dehydrogenation of small paraffins [25], aromatization of in situ generated ethylene [26], and the hydration of acetylene [27,28].

Polyhydroquinolines can be produced by MCRs catalyzed by molecular iodine [29], $HClO_4-SiO_2$ [30], trimethylsilyl chloride [31], ceric(IV) ammonium nitrate [32], L-proline [33], ionic liquids [34], silica sulfuric acid [35], Ni nanoparticles [36], metal triflates such as $Yb(OTf)_3$[37] and $Sc(OTf)_3$ [38], and Baker's yeast [39]. In addition, polyhydroquinoline MCRs can be performed by solid phase organic synthesis [40] and without a catalyst [41]. While each of these methods has some merits, they also often have low yields, a complicated work-up, use toxic and flammable solvents, are corrosive, and cause effluent pollution. To overcome these problems, a simple method that uses an eco-friendly and reusable catalyst under less hazardous conditions is required. In this manuscript, we report a highly efficient route for the synthesis of polyhydroquinolines using an inexpensive ZnO-beta zeolite as a catalyst.

2 Experimental

2.1 General

All chemicals were purchased from Merck or S.D. Fine Chem Ltd. (India) and used without further purification. Thin layer chromatography was performed on precoated silica gel 60-F254 plates (Merck). Powder X-ray diffraction (XRD) patterns of the catalysts were recorded using a X-ray diffractometer (Bruker 8D Advance) with CuKα radiation ($\lambda = 1.54056$ Å). Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT-IR-4100 (Japan). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed with a JEOL JSM-6330 operated at 20.0 kV and 1.0000 nA. Temperature programmed desorption (TPD) measurements were carried out on a Quantachrome CHEMBET 3000 TPR/TPD, and the Brunnauer–Emmett–Teller (BET) surface area was measured by N_2 adsorption at 77 K. Melting points were measured in an open capillary and not corrected. Microwave irradiation was carried out in a microwave oven (BPL, 800T, 2,450 MHz) with power output of 800 W.

3 Preparation of Catalyst

In a typical synthesis, tetraethyl orthosilicate (TEOS), was added to a mixture of tetraethyl ammonium hydroxide (TEAOH), sodium hydroxide (NaOH), and an aqueous solution of aluminum sulfate ($Al_2(SO_4)_3$), and stirred at room temperature for 24 h. This mixture was then hydrothermally treated at 120°C for 96 h in an autoclave bottle. The mixture was then cooled to room temperature, and the solid material that precipitated out was isolated by filtration and washed with deionized water. The solid was then dried at 80°C for 6 h, and calcined at 550°C for 12 h. The H-form of beta zeolite was prepared by ion exchange of the above sample with 1 mol/L ammonium acetate at 80°C for 10 h. The ion exchange procedure was repeated twice and the resulting product was calcined at 550°C for 8 h. The product was mixed with an aqueous solution of zinc acetate to modify the H-beta zeolite. The mixture was digested at 80°C for 8 h, dried, and calcined at 550°C for 8 h.

3.1 Catalyst Characterization

3.1.1 XRD Analysis

The XRD patterns of H-beta and ZnO-beta zeolite (Fig. 1) showed typical diffraction peaks of beta zeolite ($2\theta = 7.8°$ and $22.3°$) when compared with a reference spectrum [42]. The peaks of ZnO-beta zeolite were lower in intensity than the peaks of H-beta zeolite. Otherwise, there were no visible differences between the synthetic H-beta zeolite and ZnO-beta zeolite.
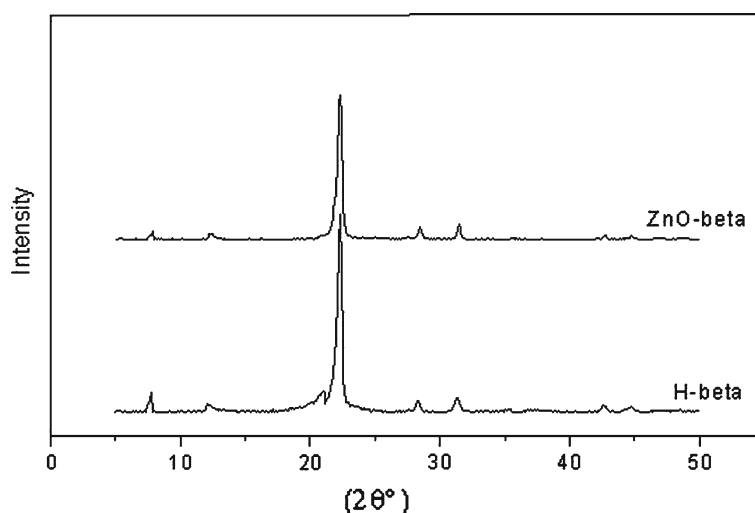
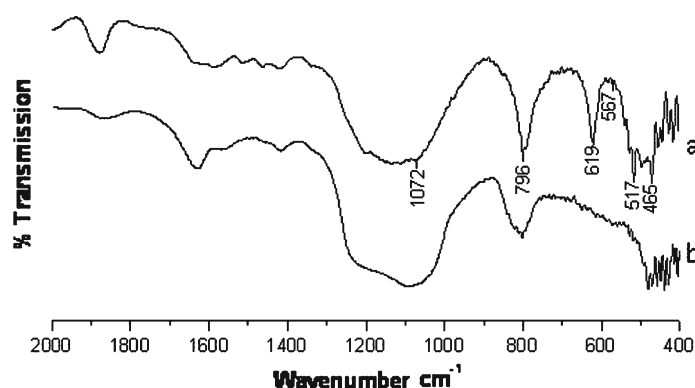**Fig. 1** XRD patterns of H-beta zeolite and ZnO-beta zeolite

Fig. 2 FT-IR spectra of **a** H-beta zeolite and **b** ZnO-beta zeolite

3.1.2 FT-IR Analysis

The FT-IR spectra of H-beta zeolite and ZnO-beta zeolite are shown in Fig. 2. The synthesized material showed IR bands around 550–650 cm^{-1}, which usually indicates the presence of zeolite-like material. The peaks at around 567 and 517 cm^{-1} could be assigned to H-beta zeolite by comparison to a reference spectrum (575 and 525 cm^{-1}) [43]. Characteristic vibrations of H-beta zeolite were also observed at around 465 and 427 cm^{-1}.

3.1.3 SEM–EDS Analysis

SEM images of H-beta zeolite and ZnO-beta zeolite are presented in Fig. 3. Interconnected porous structures formed by agglomeration of tiny particles ($< 10\mu$m) of ZnO on the H-beta zeolite crystals were observed for ZnO-beta zeolite (Fig. 3b). The mass fraction of zinc in the ZnO-beta zeolite was determined at 2.75% by EDS (Fig. 4).

3.1.4 TPD and BET Analysis

For TPD measurements, the samples were pre-treated by heating from room temperature to 200°C under nitrogen gas flow. Ammonia was then adsorbed onto the sample at room temperature. The sample was then heated from room temperature to 700°C at 10°C/min, and desorption of the adsorbed ammonia was monitored.
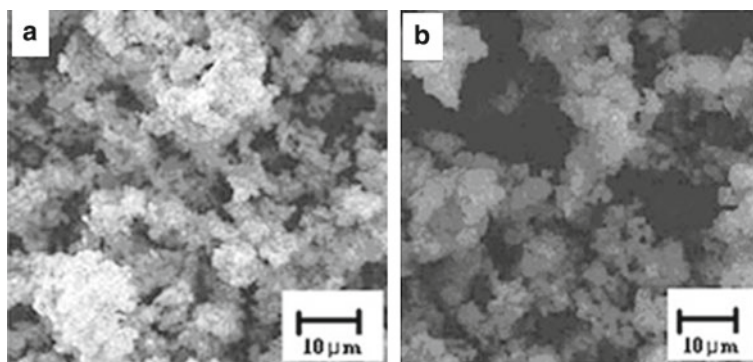
Fig. 3 SEM micrographs of **a** H-beta zeolite and **b** ZnO-beta zeolite
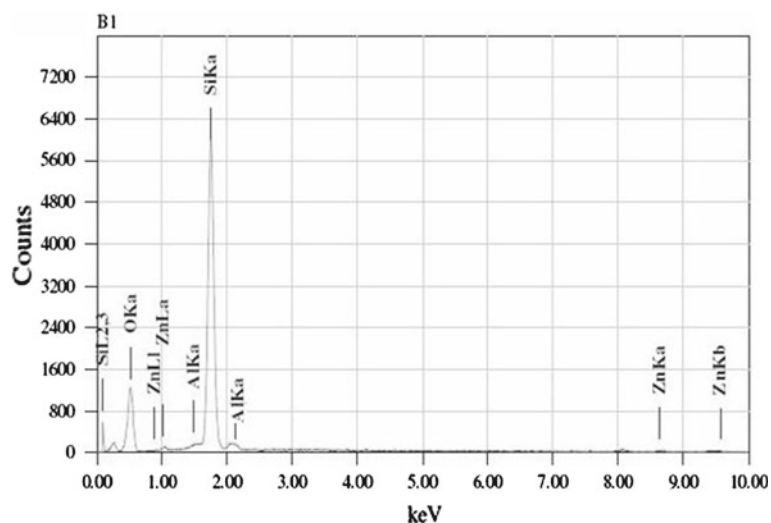

Fig. 4 EDS spectrum of ZnO-beta zeolite

The total acidity of the ZnO-beta zeolite was 0.703 mmol/gm and its calculated BET specific surface area was 137 m^2/g.

## 4 General Procedure for the Synthesis of Polyhydroquinolines

A mixture of aldehyde (2 mmol), dimedone (2 mmol), ethyl acetoacetate (2 mmol), ammonium acetate (2.5 mmol), and ZnO-beta zeolite (0.1 g) in a 10 mL beaker was irradiated in a domestic microwave oven at 450 W until the reaction was complete. Progress of the reaction was monitored by TLC. After completion of the reaction, the resulting solid product was heated in ethanol or acetonitrile and then filtered. The filtrate was concentrated and recrystallized in ethanol to afford the desired pure product.

5 Results and Discussion

We have previously investigated zeolite catalyzed reactions for the development of novel synthetic methodology [44,45]. In the present research, ZnO-beta zeolite catalysis of the Hantzsch reaction was investigated under solvent-free conditions and microwave irradiation (Scheme 1). To the best of our knowledge, catalysis of the synthesis of polyhydroquinolines with ZnO-beta zeolite has not been reported yet.

The efficiency of the ZnO-beta zeolite catalyst (0.01 g) was systematically evaluated in a model reaction of benzaldehyde (2 mmol), dimedone (2 mmol) ethyl acetoacetate (2 mmol), and ammonium acetate (2.5 mmol).
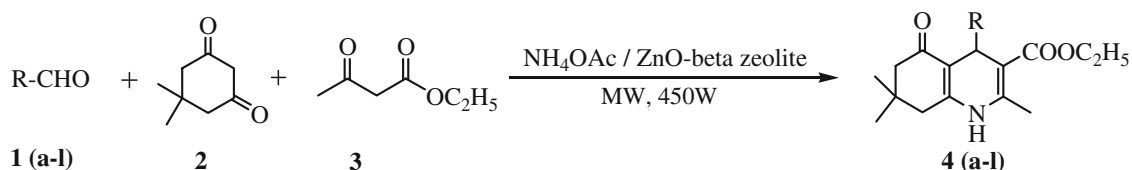
Scheme 1 Synthesis of polyhydroquinolines catalyzed by ZnO-beta zeolite

Table 1 Effect of the amount of catalyst on synthesis of ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-phenylquinoline-3-carboxylate (Table 3, compound **4a**)

Entry	Catalyst (g)	Time (min)	Yield (%)[a]
1	None	10	0
2	0.01	4	45
3	0.05	2	78
4	0.1	1.5	96 (96, 96, 95, 94)[b]
5	0.2	1.5	96

All reactions are carried out under microwave irradiation at 450 W
[a] Isolated yields
[b] The yields obtained after the catalyst was sequentially reused four times

Table 2 Effect of microwave power on synthesis of ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-phenylquinoline-3-carboxylate (Table 3, compound **4a**)

Entry	Power (W)	Time (min)	Yields (%)[a]
1	150	1.5	42
2	300	1.5	57
3	450	1.5	96
4	600	1.5	86

All reactions carried out using 0.1 g ZnO-beta zeolite
[a] Isolated yields

Ethyl-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-phenylquinoline-3-carboxylate (**4a**) was produced in 45% yield within 4 min (Table 1, Entry 2). When the catalyst loading was increased to 0.05 g, the yield of **4a** increased to 78% (Table 1, Entry 3). The yield of **4a** increased to 96% when the catalyst amount was increased to 0.1 or 0.2 g, and the reaction time reduced to 1.5 min (Table 1, Entry 4 and 5). These results indicate that 0.1 g of ZnO-beta zeolite produces the highest product yield and shortest reaction time with the lowest amount of catalyst. By contrast, in the absence of a catalyst no **4a** was produced even after 10 min (Table 1, Entry 1). This solvent free procedure has a shorter reaction time and higher yield than conventional procedures with solvents such as ethanol, methanol, or acetonitrile. ZnO-beta zeolite produced a higher yield of **4a** in a shorter reaction time than unmodified H-beta zeolite.

The effect of microwave power inputs from 150 to 600 W on the efficiency of the model reaction was investigated (Table 2). The reaction yield increased with the microwave power up to 450 W (96% yield, Table 2, Entry 3) and then decreased at 600 W (Table 2, Entry 4).

All the reactions with aldehydes **1a–l** were rapid and produced the corresponding polyhydroquinoline derivatives in good to excellent yields (Table 3). These results indicate that the method can be used with a variety of functional groups, such as methoxy, hydroxyl, nitro, and halide. High product yields were obtained with both electron-rich and electron-deficient aldehydes. The product yields were lower with aliphatic aldehydes (Table 3, Entry 4j–4l) than with the other aldehydes we investigated.

After completion of the reaction, the recovered catalyst was washed with ethyl acetate, dried at 70°C, and activated at 120°C. It was then recycled for another run of the model reaction. Excellent yields were produced with recovered catalyst in four successive reactions (Table 1, Entry 4).

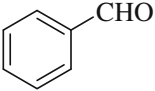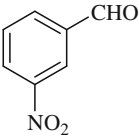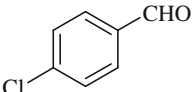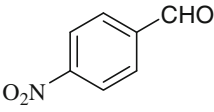**Table 3** Synthesis of polyhydroquinoline derivatives
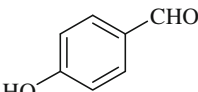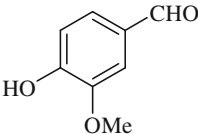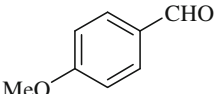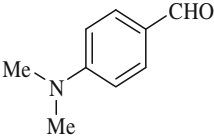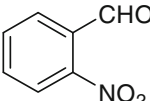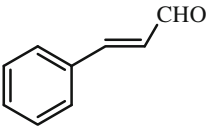
Product[a]	Reactant Aldehyde	Time (min)	Yield (%)[b]	MP (°C) Found	Lit.
4a	CHO (benzaldehyde)	1.5	96	203–204	202–205 [26]
4b	CHO, NO$_2$ (3-nitrobenzaldehyde)	5	87	176–177	176–179 [26]
4c	CHO, Cl (4-chlorobenzaldehyde)	1.5	95	230–232	232–234 [26]
4d	CHO, O$_2$N (4-nitrobenzaldehyde)	4	89	240–242	241–243 [26]
4e	CHO, HO (4-hydroxybenzaldehyde)	3	87	232–233	234–237 [26]
4f	CHO, HO, OMe (vanillin)	4	91	209–210	208–210 [26]
4g	CHO, MeO (4-methoxybenzaldehyde)	1.5	90	254–255	252–254 [26]
4h	CHO, Me–N–Me (4-dimethylaminobenzaldehyde)	2	94	228–230	228–230 [26]
4i	CHO, NO$_2$ (2-nitrobenzaldehyde)	3.5	89	210–212	208–211 [26]
4j	CHO (cinnamaldehyde)	5	84	205–206	204–206 [30]
4k	C$_2$H$_5$CHO	5	82	145–146	145–146 [30]

Table 3 continued

Product[a]	Reactant Aldehyde	Time (min)	Yield (%)[b]	MP (°C)	
				Found	Lit.
4l	$n\text{-}C_3H_7CHO$	6	81	146–147	147–148 [30]

[a] Products were characterized by comparison of their ^{1}H NMR spectra, mass spectra (Spectroscopic data for selected compounds: Ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-phenylquinoline-3-carboxylate (4a): ^{1}H NMR (80 MHz, CDCl$_3$): δ 0.94 (s, 3H), 1.09 (s, 3H), 1.14 (t, J = 7.3 Hz, 3H), 2.13–2.34 (m, 4H), 2.37 (s, 3H), 4.05 (q, J = 7.3 Hz, 2H), 5.02 (s, 1H), 5.74 (s, 1H), 7.03–7.34 (m, 5H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 14.2, 19.1, 21.3, 27.6, 36.5, 37.3, 59.8, 106.0, 113.7, 126.3, 127.8, 128.0, 143.3, 147.1, 149.2, 167.3, 194.8; IR (KBr in cm^{-1}): 3233, 3210, 3080, 1696, 1602, 1059, 692; m/z = 340 (M+H)$^+$. Ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-4-(3-nitrophenyl)-5-oxoquinoline-3-carboxylate (4b): ^{1}H NMR (80 MHz, CDCl$_3$): δ 0.96 (s, 3H), 1.04 (s, 3H), 1.22 (t, J = 7.3 Hz, 3H), 2.10-2.34 (m, 4H), 2.38 (s, 3H), 4.01 (q, J = 7.3 Hz, 2H), 4.96 (s, 1H), 6.32 (s, 1H), 6.74–7.38 (m, 4H);^{13}C NMR (75 MHz, DMSO-d$_6$) δ 14.18, 19.32, 21.1, 27.3, 33.1, 33.90, 59.5, 105.4, 112.3, 121.2, 122.8, 128.6, 134.8, 144.6, 148.3, 149.5, 151.0, 166.9, 196.0; IR (KBr in cm^{-1}): 3303, 2954, 1683, 1610, 1167, 759; m/z = 385 (M + H)$^+$. Ethyl 1,4,5,6,7,8-hexahydro-4-(4-methoxyphenyl)-2,7,7-trimethyl- 5-oxoquinoline-3-carboxylate (4g): ^{1}H NMR (80 MHz, CDCl$_3$): δ 0.96 (s, 3H), 1.06 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H), 2.10-2.26 (m, 3H), 2.34-2.40 (m, 4H), 3.77(s, 3H), 4.02 (q, J = 7.2 Hz, 2H), 5.08 (s, 1H), 5.85 (s, 1H), 6.71-7.24 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 14.3, 17.9, 26.3, 28.8, 32.4, 35.0, 50.1, 50.4, 55.1, 59.2, 102.7, 109.5, 113.4, 128.3, 128.5, 140.0, 144.9, 149.1, 156.8, 168.2, 193.8; IR (KBr in cm^{-1}): 3281, 3199, 3080, 1708, 1607, 1224, 837; m/z = 370 (M+H)$^+$) and melting points with those reported in the literature
[b] Yield refers to isolated product

6 Conclusion

A highly efficient four-component protocol catalyzed by ZnO-beta zeolite was developed for the synthesis of polyhydroquinolines without solvent under microwave irradiation. The ZnO-beta zeolite exhibits superior catalytic activity to other reported catalytic methods with respect to reaction time and amount of catalyst required. In addition, the reaction does not use hazardous solvents, has a simple work-up, and is inexpensive. The catalyst can also be recycled for subsequent reactions, with high efficiency. These characteristics make this procedure an attractive alternative to the existing methods for the synthesis of polyhydroquinolines.

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