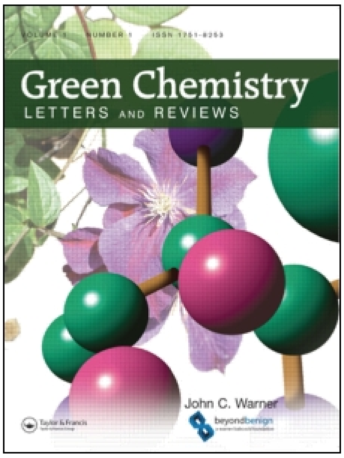

Green Chemistry Letters and Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t748292817

ZnO-beta zeolite: as an effective and reusable heterogeneous catalyst for the one-pot synthesis of polyhydroquinolines

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To cite this Article Katkar, Santosh S. , Mohite, Pravinkumar H. , Gadekar, Lakshman S. , Arbad, Balasaheb R. and Lande, Machhindra K.(2010) 'ZnO-beta zeolite: as an effective and reusable heterogeneous catalyst for the one-pot synthesis of polyhydroquinolines', Green Chemistry Letters and Reviews, 3: 4, 287 — 292

To link to this Article: DOI: 10.1080/17518253.2010.482065

URL: http://dx.doi.org/10.1080/17518253.2010.482065

Green Chemistry Letters and Reviews
Vol. 3, No. 4, December 2010, 287–292

Taylor & Francis
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RESEARCH LETTER

ZnO-beta zeolite: as an effective and reusable heterogeneous catalyst for the one-pot synthesis of polyhydroquinolines

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(Received 3 August 2009; final version received 26 March 2010)

ZnO-beta zeolite, an inexpensive and mild catalyst, has been used for the synthesis of polyhydroquinolines in excellent yields from the one-pot four-component condensation of aldehydes, dimedone, ethyl acetoacetate, and ammonium acetate in ethanol at room temperature. The remarkable advantages offered by this method are a green catalyst, mild reaction conditions, simple work-up procedures, much faster reactions, and excellent yield of products. Furthermore, the catalyst could be reused several times keeping its initial activity in recycled reactions.

Keywords: Hantzsch condensation; ZnO-beta zeolite; multicomponent; heterogeneous catalyst

Introduction

Zeolite beta is a high silica zeolite, containing an intersecting three-dimensional structure of 12-membered ring channels. Due to this relatively voluminous channel structure, it is possible to carry out numerous acid-catalyzed reactions effectively (*1*). Furthermore, zeolite beta also has adjustable acidity in the protonic form and this is another factor affecting the efficiency of reaction. Zeolite beta has been found to be a suitable transesterification catalyst to synthesize a variety of products (*2*). It is clear that the transesterification proceeds on the Bronsted acidic sites of the zeolite beta and the Bronsted acid sites of the zeolite beta also can be subtly adjusted by modification with metal cations, bringing about modified catalysts with suitable acidity to fit different transesterifications (*3–7*).

For economic and environmental reasons, the use of heterogeneous solid acid catalysts to achieve effective catalyst handling, easy isolation of products, and reusability is continuously increasing. Among the various solid acid catalysts, zeolites have received an increasing amount of attention because of their suitable acidity, thermal stability, easy work-up, recyclability, and eco-friendly nature. Zeolites have been used as catalysts in the petroleum refining and chemical industries (*8,9*). Their properties and thus, their performance as catalysts, can be adjusted by modification by ion exchange with metal ions, acid treatment, and hydrothermal treatment (*10,11*). In particular, zinc-loaded zeolites are suitable for various organic transformations, such as the Heck reaction (*12*), propane aromatization (*13*), dehydrogenation of small paraffins (*14*), aromatization of *in situ* generated ethylene (*15*), and the hydration of acetylene (*16,17*).

Heterocyclic compounds generally exhibit raised biological activity and they also make possible the development of novel materials with unique properties. An interesting and promising class of heterocycle is the 1,4-dihydropyridines (1,4-DHPs). This type of heterocycle has significant pharmacological and biological activities, such as vasodilator, bronchodilator, anti-atherosclerotic, anti-tumor, geroprotective, hepatoprotective, and antidiabetic agents (*21,22*). 1,4-DHPs are analogues of NADH coenzymes and an important class of blockers of calcium (Ca^{2+}) channel (*23,24*). These examples make clearly explicit the remarkable potential of novel currents DHPs derivatives as a source of valuable drug candidates.

Due to their great importance, many synthetic strategies have been employed for the synthesis of polyhydroquinolines, such as iodotrimethylsilane (TMSI) (*25*), $Yb(OTf)_3$ (*26*), promotion of microwave (*27*), ceric ammonium nitrate (CAN) (*28*), potassium dodeca tungsto cobaltate trihydrate (*29*), molecular iodine (*30*), $HClO_4$–SiO_2 (*31*), L-Proline (*32*), Ni-nanoparticle (*33*), montmorillonite K10 (*34*), and HY zeolite (*35*). Furthermore, many of these methods require either a long reaction time or harsh reaction conditions or the use of expensive catalyst. Therefore,

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ISSN 1751-8253 print/ISSN 1751-7192 online

DOI: 10.1080/17518253.2010.482065
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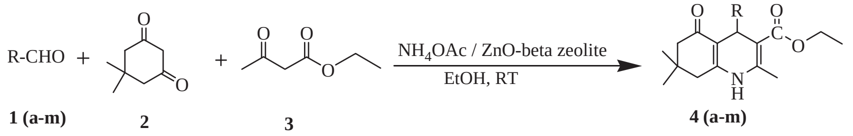

Scheme 1. Synthesis of polyhydroquinolines catalyzed by ZnO-beta zeolite at room temperature.

the development of simple, efficient, and general methodology for this one-pot four-component reaction is still desirable.

Moreover, to the best of our knowledge no report has been made about the use of zinc-modified beta zeolite as a catalyst for the Hantzsch condensation. By considering the importance of polyhydroquinolines and as a part of our ongoing investigation in developing a versatile and efficient method for synthesis of heterocyclic compounds (*36–39*). Herein, we report a very simple, fast, and general method for the synthesis of polyhydroquinolines *via* Hantzsch condensation of aldehydes, dimedone, ethyl acetoacetate, and ammonium acetate in the presence of ZnO-beta zeolite (Scheme 1).

Results and discussion

X-ray diffraction (XRD) analysis

Figure 1 depicts the X-ray diffraction (XRD) pattern of H-beta and ZnO-beta zeolite. The powder XRD pattern is the typical type for beta zeolite by comparing it with the reference beta zeolite (*40*). It was observed that, there is no visible difference between synthetic beta zeolite and zinc-modified beta zeolite. It is clear that samples contain typical diffraction peaks of H-beta zeolite ($2\theta = 7.8°$ and $22.3°$).

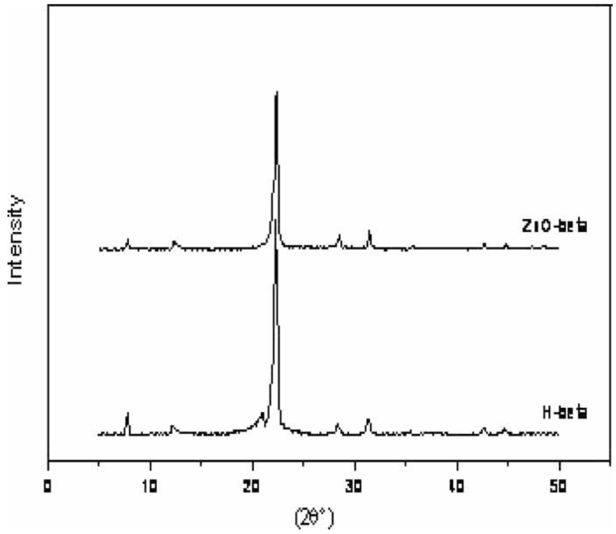

Figure 1. XRD patterns of H-beta zeolite and ZnO-beta zeolite.

Fourier transform infrared (FT-IR) analysis

The Fourier transform infrared (FT-IR) spectra of H-beta zeolite and ZnO-beta zeolite are shown in Figure 2. Synthesized material showing IR bands in the range 550–600 cm^{-1} usually indicates the presence of zeolite-like material. Peaks around 575 and 525 cm^{-1} (567 and 517 cm^{-1} in present work) correspond to H-beta zeolite (*41*). The characteristic vibrations of H-beta zeolite around 465 and 427 cm^{-1} are also observed. In zinc-modified beta zeolite only the disappearance of peak at 619 cm^{-1} is observed.

Scanning electron microscope–energy dispersive X-ray spectroscopy (SEM–EDS) analysis

The morphology of the zeolite beta and ZnO-beta zeolite are summarized in Figure 3. The scanning electron microscope (SEM) image shows that the interconnected porous structure by agglomerating of tiny particles of ZnO on H-beta zeolite crystals with an average particle size less than 10 µm (Figure 3B). From energy dispersive X-ray spectroscopy (EDS) analysis zinc content in modified beta zeolite is 2.75 mass% (Figure 4).

NH_3–temperature-programmed desorption (NH_3–TPD) and Brunnauer–Emmett–Teller (BET) analysis

Temperature-programmed desorption (TPD) measurements were carried out by (1) pre-treating of samples from room temperature to 200°C and gas flow of nitrogen; (2) adsorption of ammonia at room

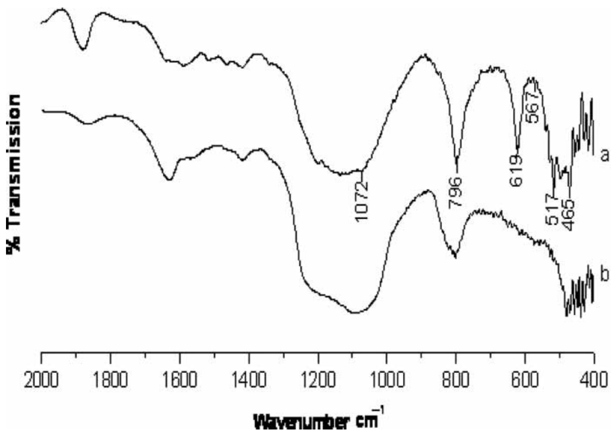

Figure 2. FT-IR spectra of H-beta zeolite (a), ZnO-beta zeolite (b).

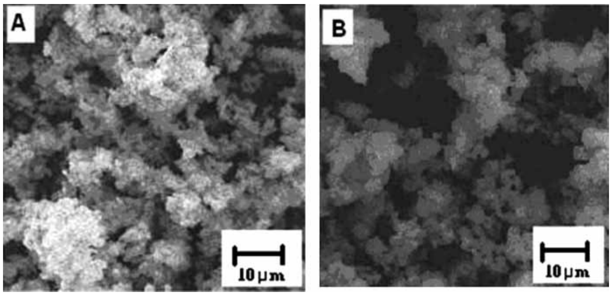

Figure 3. SEM micrograph of (A) H-beta zeolite, (B) ZnO-beta zeolite.

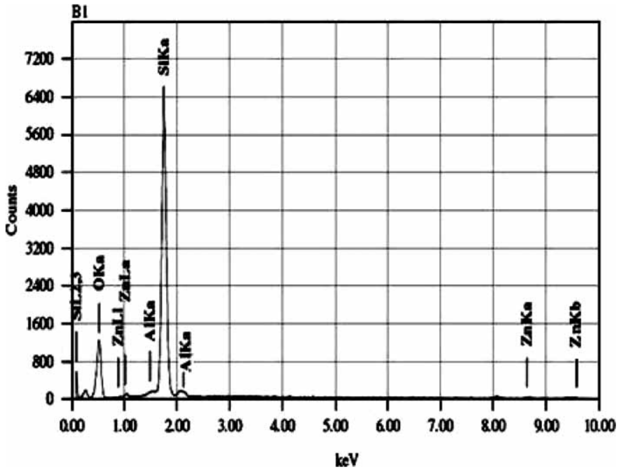

Figure 4. EDS spectrum of ZnO-beta zeolite.

temperature; (3) desorption of adsorbed ammonia with an heating rate 10°C min^{-1} starting from the adsorption temperature to 700°C. Total acidity and calculated BET surface area of ZnO-beta zeolite is summarized in Table 1.

In order to get the best experimental conditions, we initially studied the effect of various solvents and catalytic efficiency of ZnO-beta zeolite for the synthesis of ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-phenylquinoline-3-carboxylate (Table 3, entry **4a**) using the model reaction of benzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), and ammonium acetate (1.5 mmol). The reaction in acetone, toluene, and chloroform which give low yields after 5, 8, and 6 h, respectively, are given in Table 2 (entries 1–3) while acetonitrile and methanol gave moderate yield of products (Table 2, entries 4, 5). A quantitative yield of desired product was obtained in the presence of 0.1 gm of ZnO-beta zeolite within 30 min. indicating that the 0.1 gm of ZnO-beta zeolite in EtOH system is a very active catalytic system for this reaction. It is noteworthy that in the absence of catalyst, reaction gave only 18% yield at room temperature after 12 h.

With optimized reaction condition in hand, we have synthesized various polyhydroquinoline derivatives (Table 3, entries **4** (**a–m**)) *via* the condensation of substituted aldehydes with dimedone, ethyl acetoacetate, and ammonium acetate in shorter reaction times (30–60 min) with excellent yields (86–95%). This methodology avoids the use of hazardous solvents and requires only catalytic amount of the ZnO-beta zeolite to promote the reaction.

We have successfully used recovered ZnO-beta zeolite for the same model reaction and the results of recycling experiments are shown in Table 4. These results clearly indicate that the recovered ZnO-beta zeolite can be recycled successfully without significant loss of activity.

In Table 5 we compared our result with results obtained by a reported procedure for the synthesis of compound **4a**. The data presented in this table show the promising feature of this method in terms of reaction rate and the yield of product compared with that reported in the literature.

Experimental

All the chemicals were purchased from Merck, S.D. Fine India and used without further purification. Thin layer chromatography (TLC) was performed on Merck-precoated silica gel 60-F254 plates. The X-ray powder diffraction patterns of catalyst were recorded by using Bruker 8D advance X-ray diffractometer using Cu–Kα radiation of wavelength = 1.54056 Å. FT-IR spectra of catalyst were recorded on JASCO FT-IR-4100, Japan. SEM image with EDS was obtained on JEOL, JSM-6330 LA operated at 20.0 kV and 1.0000 nA. BET surface area has been measured by means of N_2 adsorption at 77 K preformed on a

Table 1. The acid strength and surface area of catalyst.

		Acidity (mmol g^{-1})[a]		
Catalyst	Total acidity (mmol g^{-1})	Weak (T_1)	Strong (T_2)	Surface area (m^2/g)[b]
ZnO-beta zeolite	0.703	0.549	0.154	137.13

[a] Desorption temperature: $T_1 = 100–300°C$, $T_2 = 300–700°C$.
[b] Calculated from BET.

Table 2. Optimization of reaction conditions for the synthesis of Ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxo-4-phenylquinoline-3-carboxylate.[a]

Entry	Solvent	Catalyst (gm)	Time	Yield (%)[b]
1	Acetone	0.1	5 h	25
2	Toluene	0.1	8 h	30
3	Chloroform	0.1	6 h	46
4	Acetonitrile	0.1	1 h	80
5	Methanol	0.1	1.5 h	72
6	Ethanol	0.1	30 min	95
7	Ethanol	0.05	50 min	88
8	Ethanol	0.2	30 min	95

[a] All reactions were carried out using ZnO-beta zeolite at room temperature.
[b] Isolated yields.

Table 4. Reusability of ZnO-beta zeolite catalyst for the synthesis of compound **4a** (Table 3, entry **4a**).[a]

Entry	1	2	3	4
Run	Fresh	First	Second	Third
Yield (%)[b]	95	95	94	93

[a] All reaction carried out at room temperature in ethanol.
[b] Isolated yields.

Quantachrome CHEMBET 3000 instrument. TPD measurements were carried out on a Quantachrome CHEMBET 3000 TPR/TPD instrument. All products are known compounds and their physical data, FT-IR, ^{1}H NMR, and mass spectra were essentially identical with those of authentic samples.

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 autoclavable bottle. After this mixture was cooled to room temperature, the solid material obtained was filtered and washed with deionised water, dried at 80°C for 6 h and calcined at 550°C for 12 h. H-form of beta zeolite was prepared through ion exchange of the above sample with 1 M ammonium acetate solution 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. Beta zeolite was modified by mixing H-form of respective zeolite with an aqueous solution of zinc acetate. The mixture was digested at 80°C for 8 h, dried and calcined at 550°C for 8 h.

Typical reaction procedure for synthesis of polyhydroquinolines

A mixture of aldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), ammonium acetate (1.5 mmol), and ZnO-beta zeolite (0.1 gm) were added in ethanol (5 mL). The reaction mixture was stirred at room temperature until the reaction was completed (monitored by TLC). After completion of the reaction, the reaction mixture was dissolved by heating, then the reaction mass filtered. The undissolved material, i.e. catalyst was washed by n-hexane (2 × 5 mL), dried at 80°C further used for next reaction (*42,43*). The filtrate was concentrated under reduced pressure and the

Table 3. Synthesis of polyhydroquinoline derivatives catalyzed by ZnO-beta zeolite.[a]

Product	*R*	Time (min)	Yield (%)	MP (°C) Found	MP (°C) Reported
4a	H	30	95	202–203	202–204 (*18*)
4b	4-$MeOC_6H_4$	30	94	257–258	257–259 (*18*)
4c	4-FC_6H_4	35	91	184–186	185–186 (*18*)
4d	4-MeC_6H_4	35	95	260–261	258–260 (*24*)
4e	4-ClC_6H_4	30	94	232–233	232–234 (*24*)
4f	2-ClC_6H_4	30	91	207–208	207–208 (*23*)
4h	4-$NO_2C_6H_4$	60	87	244–245	243–244 (*23*)
4i	3-$NO_2C_6H_4$	60	86	179–180	178–179 (*23*)
4j	2-$NO_2C_6H_4$	55	89	206–207	206–207 (*23*)
4k	4-OHC_6H_4	35	90	230–232	232–234 (*18*)
4l	2,4-$Cl_2C_6H_3$	40	91	242–244	242–243 (*18*)
4m	4-OH-3-$OCH_3C_6H_3$	45	94	210–211	208–210 (*23*)

[a] Isolated yields and melting points compared with literature data.

Table 5. Comparative data of ZnO-beta with other catalyst for the synthesis of **4a** (Table 3, entry **4a**).[a]

Entry	Catalyst/Solvent	Time	Reaction condition	Yield (%)	References
1	ZnO-beta/EtOH	30 min	Room temperature	95	Present
2	CAN/EtOH	2.0 h	Room temperature	94	(*20*)
3	Yb(OTf)$_3$/EtOH	5 h	Room temperature	90	(*18*)
4	L-Proline/EtOH	6 h	Reflux	92	(*24*)
5	HY zeolite/CH$_3$CN	2 h	Room temperature	93	(*27*)

[a]Isolated yields.

obtained solid was recrystallized from ethanol to obtain pure product.

Spectroscopic data of some 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 **(4i):** ^{1}H NMR (80 MHz, CDCl3): 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 **(4b):** ^{1}H NMR (80 MHz, CDCl3): 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)$^+$.

Conclusions

In summary, this paper describes a simple, convenient, and eco-friendly protocol for the one-pot multi-component synthesis of polyhydroquinoline derivatives in ethanol at room temperature. This method offers very attractive features, such as short reaction times (30–60 min), excellent yields, and easy work-up procedure. Moreover, the ZnO-beta zeolite was successfully reused for four cycles without significant loss of activity. It is thus a rapid, convenient work-up procedure, mild reaction conditions, inexpensive, and eco-friendly nature of the catalyst that makes this method a valid contribution to the existing methodologies.

Acknowledgements

The authors are thankful to the Head, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for providing the laboratory facility.

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