J IRAN CHEM SOC
DOI 10.1007/s13738-014-0571-y

ORIGINAL PAPER

ZnS nanoparticles as an efficient and reusable catalyst for synthesis of 4*H*-pyrano[2,3-*c*]pyrazoles

Ashok Vishram Borhade · Bhagwat Karbhari Uphade

Received: 28 July 2014 / Accepted: 6 December 2014

Abstract An efficient procedure has been reported for the synthesis of 4*H*-pyrano[2,3-*c*]pyrazoles in the presence of ZnS nanoparticles as a heterogeneous catalyst at the room temperature by grinding method. The ZnS nanoparticles were synthesized by hydrothermal method and characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and N_2 adsorption–desorption isotherm analysis. The 4*H*-pyrano[2,3-*c*]pyrazoles were obtained with high yields (87–97 %) in a short reaction time (5–21 min) under solvent-free condition. This method has advantages such as it is solvent free, uses simple grinding method that can be carried out at room temperature, requires short reaction times and production of pure products without any by product. The nanocatalyst can be easily recovered and reused for five runs without appreciable loss of its catalytic activity.

Keywords ZnS nanoparticles · 4*H*-pyrano[2,3-*c*] pyrazoles · Grinding · Solvent free condition · Catalyst reuse

Introduction

The 4*H*-pyrano[2,3-*c*]pyrazoles and their derivatives are important class of heterocyclic compounds due to their pharmacological and biological properties [1]. They are widely used in biodegradable agrochemicals and pharmaceutical ingredients [2]. Pyranopyrazoles exhibit biological properties such as anti-inflammatory, anticancer, antimicrobial and analgesic activity, and acts as a hypoglycemic, hypotensive and vasodilator agent [3–9]. The derivatives of 4*H*-pyrano[2,3-*c*]pyrazoles have an affinity toward A1 and A2a adenosine receptors [10]. They also exhibit molluscicidal activity and are used as a screening kit for Chk1 kinase inhibitor [11]. Substituted 4*H*-pyrano[2,3-*c*]pyrazole derivatives have been found to be effective antiplatelet agents [12]. Therefore, the synthesis of pyranopyrazole derivatives is recently of much interest. There are several catalysts reported for the synthesis of 4*H*-pyrano[2,3-*c*]pyrazoles including ethanol [13], absolute ethanol by heating or electrochemical method under an inert atmosphere [14, 15], boiling water [16], iodine [17], 3-methyl-1-(4-sulfonic acid) butyl imidazolium hydrogen sulfate [18], silicotungstic acid [19], water using combination of microwave and ultrasonic irradiation [20], nano-titania supported Preyssler-type heteropoly-acid [21], sodium benzoate [22], ionic liquid [23], microwave [24] and nano ZnO [25].

Recently, nanocrystalline metal oxide, metal sulfide and modified nanocatalyst have been used as catalysts in organic synthesis [26–37]. In consideration of green chemical methodology, here we report the synthesis of 4*H*-pyrano[2,3-*c*]pyrazoles derivatives using ZnS nanoparticles as a catalyst to explore the catalytic activity of nanoparticles in organic synthesis under solvent-free condition with grinding at room temperature.

Experimental

Chemicals and apparatus

All chemicals were purchased from Aldrich chemical and were used without purification. The X-ray diffraction

A. V. Borhade (✉)
Department of Chemistry and Research Center, HPT Arts and RYK Science College, Nasik 422005, India
e-mail: ashokborhade2007@yahoo.co.in

B. K. Uphade
Department of Chemistry and Research Center, P.V.P College, Pravaranagar, Ahmednagar 413713, India

Published online: 28 December 2014

(XRD) pattern was recorded using Philips-1710 diffractometer with Cu–Kα radiation (λ = 1.54 A°). The SEM with EDAX was recorded using JEOL-JEM-6360 microscope. The TEM was recorded with SAED using CM-200 Philips microscope. The surface area was recorded with help of Quantachrome Autosorb Automated Gas Sorption system. Melting points reported are determined by a melting point apparatus with open capillary tubes and are uncorrected. FTIR spectra of different products were recorded on Schimadzu 8400s spectrometer using KBr pellets. ^{1}H NMR spectra were recorded with a Bruker Advance II 400 MHz spectrometer in DMSO-d_6 with TMS as an internal standard. ^{13}C NMR spectra were recorded with a Bruker Advance II 100 MHz spectrometer. Mass spectra were recorded with a JEOL GCMATE II GC-MS instrument.

Typical experimental procedure for the synthesis of ZnS nanoparticles

The ZnS nanoparticles were synthesized by simple hydrothermal method using solution of analytical-grade high-purity zinc nitrate. In the solution of zinc nitrate (10 mmol, 2.974 g), sodium dodecyl sulfate was added as a capping agent (2 mmol, 0.576 g) while sodium sulfide (10 mmol, 0.780 g) was slowly added and the reaction mixture was stirred for 5 h. The reaction mixture was filtered and nanocrystalline zinc sulfide material was dried in an oven at 120 °C for 2 h. The zinc sulfide nanocrystal was further calcinized at 400 °C for 2 h. The calcined ZnS nanoparticles were used as catalyst.

Typical experimental procedure for the synthesis of 4*H*-pyrano[2,3-*c*]pyrazoles

To a mixture of hydrazine hydrate (1.0 mmol, 0.050 g) and ethyl acetoacetate (1.0 mmol, 0.130 g), ZnS nanoparticles (0.5 mmol, 0.050 g) were added and stirred for few minutes. Then, benzaldehyde (1.0 mmol, 0.106 g) and malononitrile (1.0 mmol, 0.066 g) were added to it and the reaction mixtures were ground by mortar and pestle at room temperature. The reaction was monitored by thin-layer chromatographic technique. After completion of the reaction, the crude product was recrystallized from hot ethanol to afford the pure products. A series of 4*H*-pyrano[2,3-*c*]pyrazoles were synthesized in high yields (**5a**–**h**). The catalyst was separated by filtration, dried at 110 °C for 2 h and reused for similar reaction. The spectral data IR, ^{1}H NMR, ^{13}C NMR and MS of all synthesized compounds are reported [16–25]. The physical and spectroscopic data of the synthesized compounds are shown below.

Spectroscopic data

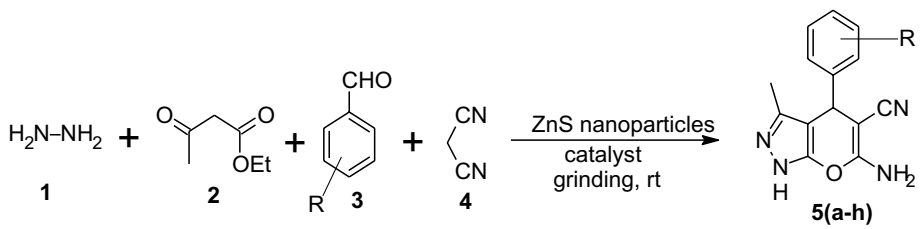
Compound (Table 3, 5a): IR (KBr, cm^{-1}): 3,370, 3,307, 2,190, 1,609, 1,591, 1,441; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 1.78 (s, 3H, CH_3), 4.58 (s, 1H, C-4), 6.85 (s, 2H, NH_2), 7.15–7.33 (m, 5H, Ar–H), 12.08 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO, δ): 9.71, 36.24, 57.15, 97.56, 120.75, 126.67, 127.43, 128.36, 135.51, 144.39, 154.72, 160.82; MF: $C_{14}H_{12}N_4O$; MW: 252; MS (*m/z*): 253 $(M+1)^+$.

Compound (Table 3, 5b): IR (KBr, cm^{-1}): 3,381, 3,288, 2,192, 1,626, 1,510, 1,451; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 1.81 (s, 3H, CH_3), 4.95 (s, 1H, C-4), 6.91 (s, 2H, NH_2), 7.40–7.46 (m, 2H, Ar–H), 7.75 (d, 1H, Ar–H, $J = 8.40$ Hz), 7.87 (s, 1H, Ar–H), 12.11 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO, δ): 9.71, 32.0, 59.1, 98.1, 121.8, 124.1, 127.2, 130.5, 134.6, 135.1, 141.2, 145.8, 147.5, 165.1; MF: $C_{14}H_{11}N_5O_3$; MW: 297; MS (*m/z*): 298 $(M+1)^+$.

Compound (Table 3, 5c): IR (KBr, cm^{-1}): 3,471, 3,278, 3,114, 2,191, 1,648, 1,598, 1,508, 1,489; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 1.78 (s, 3H, CH_3), 4.87 (s, 1H, C-4), 7.41 (d, 2H, Ar–H, $J = 8.70$ Hz), 7.43 (s, 2H, NH_2), 8.25 (d, 2H, Ar–H, $J = 8.70$ Hz), 12.21 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO, δ): 9.3, 35.1, 96.1, 120.7, 123.2, 128.1, 135.3, 146.7, 151.3, 154.2, 161.3; MF: $C_{14}H_{11}N_5O_3$; MW: 297; MS (*m/z*): 298 $(M+1)^+$.

Compound (Table 3, 5d): IR (KBr, cm^{-1}): 3,409, 3,368, 2,192, 1,515, 1,450; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 1.62 (s, 3H, CH_3), 4.97 (s, 1H, C-4), 6.83 (s, 2H, NH_2), 6.96–7.88 (m, 4H, Ar–H), 11.96 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO, δ): 10.3, 27.4, 57.6, 97.6, 121.7, 130.3, 135.3, 137.2, 138.2, 148.7, 156.3, 161.3; M. F: $C_{14}H_{11}BrN_4O$; M. W: 331; MS (*m/z*): 332 $(M+1)^+$.

Compound (Table 3, 5e): IR (KBr, cm^{-1}): 3,478, 3,247, 2,180, 1,596, 1,448; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 1.74 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 4.64 (s, 1H, C-4), 6.81 (d, 2H, Ar–H, $J = 8.20$ Hz), 6.82 (d, 2H, Ar–H, $J = 8.20$ Hz), 7.12 (s, 2H, NH_2), 12.13 (s, 1H, NH); ^{13}C



Scheme 1 synthesis of 4*H*-pyrano[2,3-*c*]pyrazoles

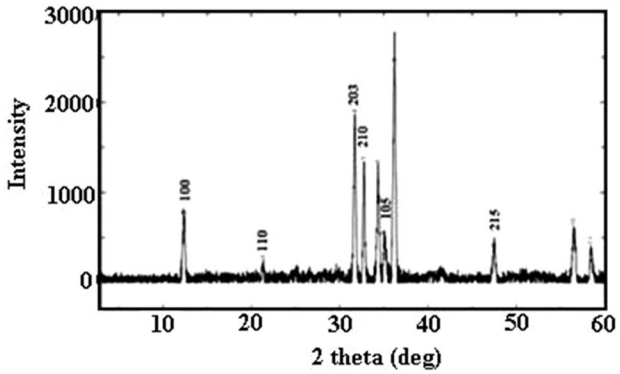


Fig. 1 X-ray diffraction pattern of synthesized ZnS nanoparticles

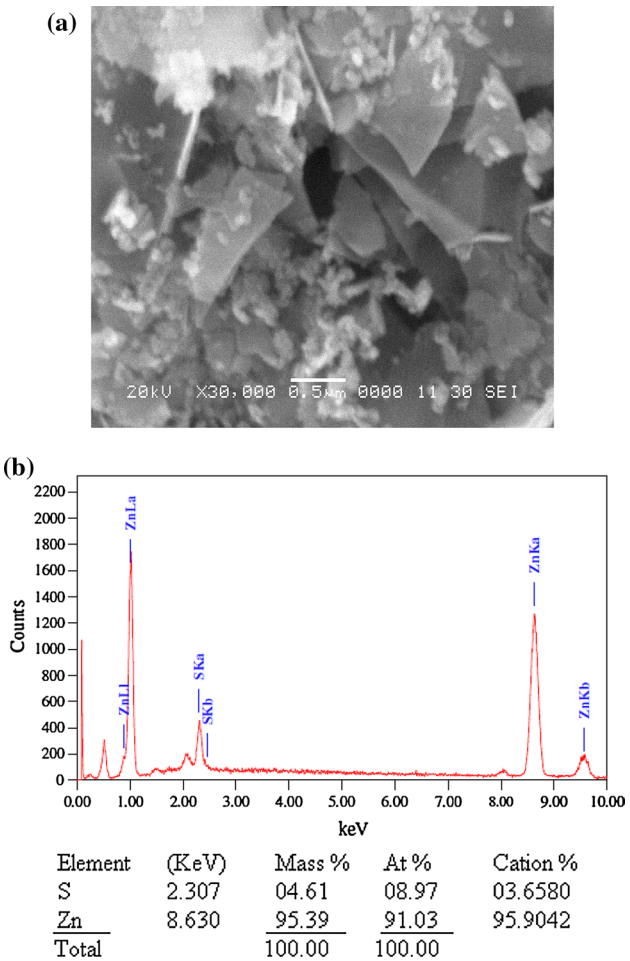


Fig. 2 **a** SEM of ZnS nanoparticles **b** EDAX of ZnS nanoparticles

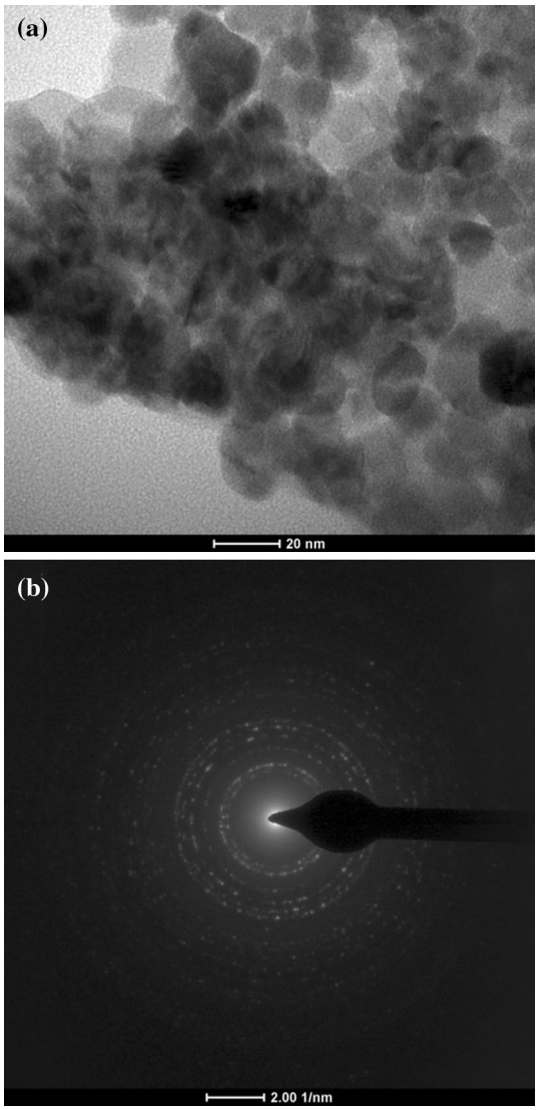


Fig. 3 **a** TEM of ZnS nanoparticles **b** SAED of ZnS nanoparticles

NMR (100 MHz, DMSO, δ): 10.5, 36.7, 54.7, 57.2, 107.8, 112.8, 114.8, 118.1, 136.2, 144.7, 155.1, 156.6, 160.1; MF: $C_{15}H_{14}N_4O_2$; MW: 282; MS (*m/z*): 283 $(M+1)^+$.

Compound (Table 3, 5f): IR (KBr, cm^{-1}): 3,412, 3,371, 2,184, 1,598, 1,482; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 1.76 (s, 3H, CH_3), 2.24 (s, 3H, Ar-CH_3), 4.56 (s, 1H, C-4), 6.80 (s, 2H, NH_2), 7.06 (d, 2H, Ar–H, J = 8.0 Hz), 7.13 (d, 2H, Ar–H, J = 8.0 Hz), 12.10 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO, δ): 9.5, 20.5, 35.7, 57.6, 97.2, 118.6, 120.1, 124.3, 128.5, 135.2, 141.7, 154.3, 160.6; MF: $C_{15}H_{14}N_4O$; MW: 266; MS (*m/z*): 267 $(M+1)^+$.

Compound (Table 3, 5g): IR (KBr, cm^{-1}): 3,374, 3,305, 2,182, 1,595, 1,492; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 1.78 (s, 3H, CH_3), 4.46 (s, 1H, C-4), 6.70 (d, 2H, Ar–H, J = 8.30 Hz), 6.81 (s, 2H, NH_2), 6.97 (d, 2H, Ar–H, J = 8.30 *Hz*), 9.25 (s, 1H, OH), 12.06 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO, δ): 9.6, 35.5, 57.7, 97.7, 115.2, 120.6, 128.4, 134.3, 135.3, 154.6, 155.8, 160.4; M. F: $C_{14}H_{12}N_4O_2$; M. W: 268; MS (*m/z*): 269 $(M+1)^+$.

Compound (Table 3, 5 h): IR (KBr, cm^{-1}): 3,372, 3,225, 2,183, 1,621, 1,520, 1,486; ^{1}H NMR (400 MHz, DMSO-d_6,

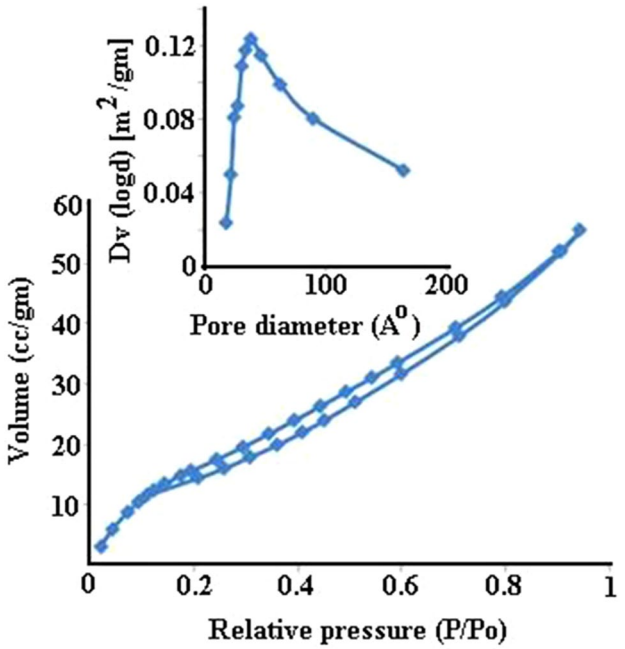


Fig. 4 BET surface area of ZnS nanoparticles

Table 1 Effect of amount of catalyst

Entry	Catalyst amount (g)	Time (min)	Yield (%)
1	0.010	24	80
2	0.020	20	82
3	0.030	15	85
4	0.040	10	88
5	0.050	8	92
6	0.060	8	92
7	0.070	8	92

δ): 1.80 (s, 3H, CH_3), 4.63 (s, 1H, C-4), 6.91 (s, 2H, NH_2), 7.22 (d, 2H, Ar–H, $J = 8.30$ *Hz*), 7.35 (d, 2H, Ar–H, $J = 8.30$ *Hz*), 12.12 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO, δ): 9.7, 35.4, 57.1, 97.2, 120.2, 128.4, 129.1, 131.2, 135.4, 143.5, 154.4, 160.6; M. F: $C_{14}H_{11}ClN_4O$; M. W: 287; MS (*m/z*): 288 $(M+1)^+$.

Results and discussion

Characterization of the ZnS nanoparticles

The ZnS nanoparticles synthesized by hydrothermal method and were characterized by different analytical techniques. The X-ray diffraction (XRD) patterns of ZnS nanoparticles (Fig. 1) have peaks due to the crystal plane 100, 105, 110, 203, 210 and 215. The X-ray diffraction (XRD) pattern of synthesized ZnS nanoparticles shows single-phase system with average crystallite size of 20 nm. The peak at 32.3, 33.5 and 47.6 is used for determining the average crystalline size of ZnS nanoparticles from XRD pattern. The X-ray diffraction (XRD) pattern is in agreement with hexagonal structure of ZnS nanoparticles (JCPDS Card no. 01-0677).

Table 2 Screening of catalyst for the synthesis of 4*H*-pyrano[2, 3-*c*] pyrazoles [16–25]

Entry	Catalyst	Time (min)	Yield (%)	Temperature (°C)
1	None	180	No reaction	60
2	$FeCl_3$	10	20	60
3	$SnCl_4$	10	38	60
4	$ZnCl_2$	10	25	60
5	P_2O_5	10	32	60
6	CAN	10	15	60
7	$H_4[SiW_{12}O_{40}]$	10	96	60
8	Nano ZnO	90	87	70
9	Water: ethanol	120	90	Reflux
10	[bmim]OH	5	85	60
11	Microwave	5	76	–
12	Ionic liquid	30	85	Room temperature
13	Sodium benzoate	50	85	Room temperature
14	Iodine	10	90	Room temperature
15	Bulk ZnS	50	45	Room temperature
16	ZnS nanoparticles	10	94	Room temperature

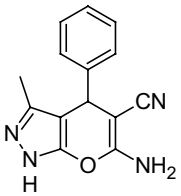
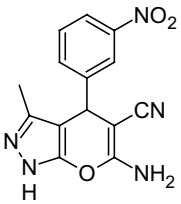
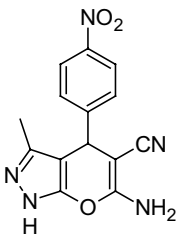
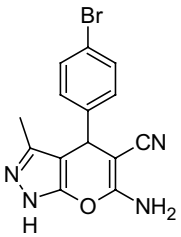
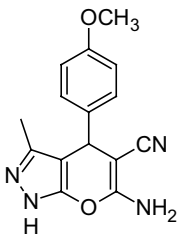
Reaction conditions ethyl acetoacetate (1.0 mmol), hydrazine hydrate (1.0 mmol), 3-nitro benzaldehyde (1.0 mmol) and malononitrile (1.0 mmol), solvent free in the presence of ZnS nanoparticles

The scanning electron microscopy (SEM) image confirms the hexagonal structure of ZnS nanoparticles with uniform shape and size (Fig. 2a). The EDAX spectrum (Fig. 2b) shows the elemental analysis of ZnS nanoparticles and the presence of Zn and S element in the synthesized sample material.

The transmission electron microscopy (TEM) analysis (Fig. 3a) reveals that nanomaterial is of hexagonal structure. The dark spot in the SAED (Fig. 3b) reveals the occurrence of hexagonal ZnS in the total agreement with XRD data. The transmission electron microscopy (TEM) analysis confirms that the average crystallite size of ZnS nanoparticles is about 20 nm.

The N_2 adsorption–desorption isotherms and BJH pore size distribution of ZnS nanoparticles (Fig. 4) show that the samples have typical IV N_2 adsorption–desorption isotherm with specific surface area (S_{BET}) obtained from BET method as 84.71 m^2/g; the average pore volume (V_p) and pore diameter (d_p) are 0.0865 cc/g and 31.11 Å.

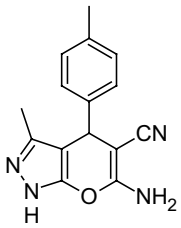
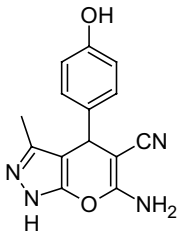
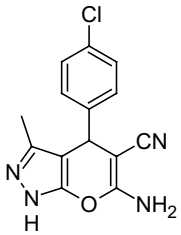
Table 3 Synthesis of 4*H*-pyrano[2,3-*c*]pyrazoles in the presence of ZnS nanoparticles

Entry	R	Product	Time (min)	Yield (%)	M. P (^{o}C)
1	H	 **5a**	8	92	244
2	3-NO_2	 **5b**	10	94	193
3	4-NO_2	 **5c**	5	97	195
4	4-Br	 **5d**	11	96	206
5	4-OCH_3	 **5e**	21	88	211

Catalytic reaction for synthesis of 4*H*-pyrano[2,3-*c*] pyrazoles

In continuation of our research on the synthesis of heterocyclic molecules using nanoparticles for cyclization and condensation reactions [38–42], we report the synthesis of 4*H*-pyrano[2,3-*c*]pyrazoles by grinding under solvent-free condition and using ZnS nanoparticles at room temperature. In the synthesis of 4*H*-pyrano[2,3-*c*]pyrazoles to optimize the amount of catalyst, the model reaction of

continued

Entry	R	Product	Time (min)	Yield (%)	M. P (^{o}C)
6	4-CH_3	 **5f**	20	87	202
7	4-OH	 **5g**	16	93	225
8	4-Cl	 **5h**	20	96	175

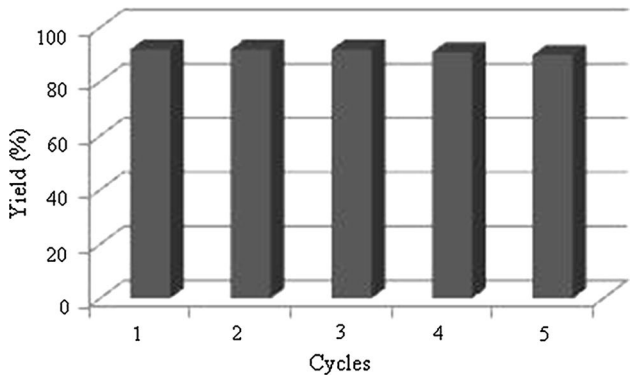


Fig. 5 Recycling of ZnS nanoparticles catalyst

benzaldehyde, hydrazine hydrate, ethyl acetoacetate and malononitrile (Scheme 1) was carried out with different amounts of ZnS nanoparticle catalysts such as 0.010, 0.020, 0.030, 0.040, 0.050, 0.060, 0.070 g. The 0.050 g of ZnS nanoparticles was sufficient to promote the reaction and greater amount of the ZnS nanoparticles did not improve the yields (Table 1). In heterogeneous catalysis, the surface area of the catalyst plays important role, determines the availability of catalytic sites and directs the reaction to take place. The surface area of 0.050 g ZnS nanoparticles was sufficient to convert reactants into the product. Therefore, the amount of the ZnS nanoparticles above the 0.050 g does not improve the yields.

To compare the efficiency of the ZnS nanoparticles catalyst for the synthesis of 4*H*-pyrano[2, 3-*c*]pyrazoles to improve the yield and to optimize the reaction conditions, it is compared with the another catalysts [16–25]. An efficient reaction was observed with high yield in the presence of ZnS nanoparticles under solvent-free condition at room temperature with grinding method (Table 2). Bulk ZnS is used to carry out same model reaction, but requires more time and gives fewer yields.

After optimizing the reaction conditions a variety of aromatic aldehydes with hydrazine hydrate, ethyl acetoacetate and malononitrile were employed under same reaction conditions to evaluate the scope of this reaction. A series of

4*H*-pyrano[2,3-*c*]pyrazoles were prepared using ZnS nanoparticles as a catalyst (Table 3) with excellent yields at room temperature with grinding and at solvent-free condition. The reaction proceeds efficiently by either electron releasing or electron withdrawing substituents on aryl ring of aldehyde. In case of aromatic aldehydes, the nature of substituents of aromatic aldehydes did not have appreciable effect on overall yields of the product. The electron-deficient aldehydes gave excellent yield of products. The position (o, m and p) of the substituted aromatic aldehydes did not show any noticeable effect on either the reaction time or the yields.

The catalyst was filtered after completion of the reaction and washed with ethanol and heated at 120 °C in oven for 2 h. The recovered catalyst was further used in several successive runs under identical reaction condition. The catalyst exhibited a good catalytic activity and stable was even after five runs (Fig. 5).

Conclusions

The ZnS nanoparticles were successfully synthesized by hydrothermal method and were characterized by different analytical techniques. We have also developed a green chemistry approach for one-pot synthesis of 4*H*-pyrano[2,3-*c*] pyrazoles using ZnS nanoparticles as an efficient catalyst by grinding at room temperature. The advantages of this protocol are simple work-up, excellent yield, solvent-free reaction and utilization of nanoparticles as a reusable catalyst.

Acknowledgments The authors are thankful to CSIR, New Delhi for the financial assistance (01/2745/13/EMR-II) and Savitribai Phule Pune University as well as Sophisticated Analytical Instrument Facility (SAIF), Punjab University, Chandigarh for providing spectral analysis facilities. Authors are also thankful to Dr. Anil G. Gadhave for his helpful suggestions.

References

1. G.A. Nawwar, F.M. Abdelrazek, R.H. Swellam, Arch. Pharm. (Weinheim) **324**(11), 875 (1991)
2. V.Y. Sosnovskikh, M.A. Barabanov, B.I. Usachev, R.A. Irgashev, V.S. Moshkin, Russ. Chem. Bull. Int. Ed. **54**(12), 2846 (2005)
3. T. Ueda, H. Mase, N. Oda, I. Ito, Chem. Pharm. Bull. (Tokyo) **29**(12), 3522–3528 (1981)
4. L.J. Huang, M.J. Hour, C.M. Teng, S.C. Kuo, Chem. Pharm. Bull. (Tokyo) **40**(9), 2547–2551 (1992)
5. P.T. Mistry, N.R. Kamdar, D.D. Haveliwala, S.K. Patel, J. Heterocycl. Chem. **49**, 349 (2012)
6. A.H. Mandour, E.R. El-Sawy, M.S. Ebaid, S.M. Hassan, Acta. Pharm. **62**, 15 (2012)
7. J.L. Wang, D. Liu, Z.J. Zheng, S. Shan, X. Han, S.M. Srinivasula, C.M. Croce, E.S. Alnemri, Z. Huang, Proc. Natl. Acad. Sci. USA **97**, 7124 (2009)
8. M.E.A. Zaki, E.M. Morsy, F.M. Abdel-Motti, F.M.E. Abdel-Megeid, Heterocycl. Commun. **10**, 97 (2004)
9. S.R. Mandha, S. Siliveri, M. Alla, V.R. Bommena, M.R. Bommineni, S. Balasubramanian, Bioorg. Med. Chem. Lett. **22**, 5272 (2012)
10. D. Catarzi, L. Cecchi, V. Colotta, G. Filacchioni, C. Martini, P. Tacchi, A. Lucacchini, J. Med. Chem. **38**(8), 1330 (1995)
11. A. Shaabani, A. Sarvary, A.H. Rezayan, S. Keshipour, Tetrahedron **65**, 3492 (2009)
12. S.M. Yu, S.C. Kuo, L.J. Huang, S.S. Sun, T.F. Huang, C.M. Teng, J. Pharm. Pharmacol. **44**(8), 667 (1992)
13. H.H. Otto, H. Schmelz, Arch. der Pharm. **312**(6), 478 (1979)
14. A.M. Shestopalov, Y.M. Emeliyanova, A.A. Shestopalov, L.A. Rodinovskaya, Z.I. Niazimbetova, D.H. Evans, Org. Lett. **4**, 423 (2002)
15. A.M. Shestopalov, Y.M. Emeliyanova, A.A. Shestopalov, L.A. Rodinovskaya, Z.I. Niazimbetova, D.H. Evans, Tetrahedron **59**, 7491 (2003)
16. M. Bihani, P.P. Bora, G. Bez, J. Chem. (2013). doi:10.1155/2013/920719
17. M.B.M. Reddy, M.A. Pasha, Indian J. Chem. **51B**, 537 (2012)
18. J. Ebrahimi, A. Mohammadi, V. Pakjoo, E. Bahramzade, A. Habibi, J. Chem. Sci. **124**(5), 1013 (2012)
19. H.V. Chavan, S.B. Babar, R.U. Hoval, B.P. Bandgar, Bull. Korean Chem. Soc. **32**(11), 3963 (2011)
20. Y. Peng, G. Song, R. Dou, Green. Chem. **8**, 573 (2006)
21. D. Azarifer, S.M. Khatami, R. Nejat-Yami, J. Chem. Sci. **126**(1), 95 (2014)
22. H. Kiyani, H.A. Samimi, F. Ghorbani, S. Esmaieli, Curr. Chem. Lett. **2**, 197 (2013)
23. J.M. Khurana, A. Chaudhary, Green Chem. Lett. Rev. **5**(4), 633 (2012)
24. H.G. Kathrotiya, R.G. Patel, M.P. Patel, J. Serb. Chem. Soc. **77**(8), 983 (2012)
25. S.U. Tekale, S.S. Kauthale, K.M. Jadhav, R.P. Pawar, J. Chem. (2013). doi:10.1155/2013/840954
26. L. L. Chng, N. Erathodiyil, J. Y. Ying, Acc. Chem. Res. doi:10.1021/ar300197s
27. H. Naeimi, Z. Nazifi, J. Nanopart. Res. **15**, 2026 (2013)
28. F. Zaera, Chem. Soc. Rev. **42**, 2746 (2013)
29. S.S. Kahandal, S.R. Kale, M.B. Gawande, R.V. Jayaram, Catal. Sci. Technol. **4**, 672 (2014)
30. R. Hudson, Y. Feng, R.S. Varma, A. Moores, Green Chem. **16**, 4493 (2014)
31. S.N. Shelke, S.R. Bankar, G.R. Mhaske, S.S. Kadam, D.K. Murade, S.B. Bhorkade, A.K. Rathi, N. Bundaleski, O.M.N.D. Teodoro, R. Zboril, R.S. Varma, M.B. Gawande, ACS. Sustain. Chem. Eng. **2**(7), 1699 (2014)
32. R.S. Varma, Sustain. Chem. Process. **2**, 11 (2014)
33. G. Li, Z. Tang, Nanoscale **6**, 3995 (2014)
34. Y. Imada, M. Ohsaki, M. Noguchi, T. Maeda, M. Fujiki, S. Kawamorita, N. Komiya, T. Naota, Chem. Cat. Chem. doi:10.1002/cctc.201402619
35. J. Yigang, W. Lei, F. Qinghua, Acta. Chim. Sin. **72**(7), 798 (2014)
36. A. Dandia, V. Parewa, A.K. Jain, K.S. Rathore, Green Chem. **13**, 2135 (2011)
37. E. Mohsen, J. Jaber, M.A. Mehdi, N.D. Fatemeh, J. Iran. Chem. Soc. **11**, 499 (2014)
38. A.V. Borhade, B.K. Uphade, D.R. Tope, J. Chem. Sci. **125**(3), 583 (2013)
39. A. V. Borhade, D. R. Tope, S. G. Gite, Arabian J. Chem. doi:10.1016/j.arabjc.2012.11.001
40. A.V. Borhade, B.K. Uphade, D.R. Tope, Res. Chem. Intermed. **40**(1), 211 (2014)
41. A. V. Borhade, B. K. Uphade, A. G. Gadhave, In press. Res. Chem. Intermed. doi:10.1007/s 11164-013-1284-z
42. A.V. Borhade, D.R. Tope, D.R. Patil, J. Chem. Pharm. Res. **4**(5), 2501 (2012)