

Efficient one-pot synthesis of pyrazoles catalyzed by nano-crystalline solid acid catalyst

Abbas Teimouri^{a*}, Alireza Najafi Chermahini^b, Leila Ghorbanian^c

^a Chemistry Department, Payame Noor University, 19395-4697, Tehran, Iran.

^b Department of Chemistry, Isfahan University of Technology, Isfahan, 841543111, Iran.

^c Materials Engineering Department, Isfahan University of Technology, Isfahan, Iran.

Received 11 October 2013; received in revised form 16 November 2013; accepted 17 December 2013

ABSTRACT

An efficient and green protocol for the synthesis of pyrazoles derivatives by one-pot reaction of different 1,3-dicarbonyl compounds with hydrazines/hydrazides has been developed using nano-sulfated zirconia, nano-structured ZnO, nano- γ -alumina and nano-ZSM-5 zeolites, as the catalyst. The optical properties of the nano-structured catalysts and organic molecules were studied. The advantages of methods are short reaction times and milder conditions, easy work-up and purification of products by non-chromatographic methods. The catalysts can be recovered for subsequent reactions and reused without any appreciable loss of efficiency.

Keywords: Nano-sulfated zirconia, Nano ZnO, Nano- γ -alumina, Nano-ZSM-5, Green synthesis, Pyrazoles.

1. Introduction

Pyrazole derivatives have become increasingly important in the past few years because they have proven to be extremely useful intermediate for the preparation of new biological materials. The pyrazole ring is present in numerous pharmacological compounds [1-4].

Many procedures for the synthesis of pyrazoles derivatives have been developed during the last two decades [5]. But the most efficient method of choice is the reaction of 1,3-diketones with hydrazines and their derivatives [6, 7].

Other methods for the synthesis of pyrazole that do not require 1,3-diketones have been reported [8-11]. Till now reactions between 1,3-diketones and hydrazines with sophisticated catalyst such as amberlyst-70 [12], PSSA [13], saponites [14], $K_2CO_3/[Cp^*IrCl_2]_2$ [15], $Zn[(L)proline]_2$ [16], $Al_2O_3/montmorillonite$ [17], $H_3PW_{12}O_{40}$ [18], Zirconium sulfophenylphosphonate [19], $CsF-Al_2O_3$ & $KOH-Al_2O_3$ [20], $CsF-Celite$ [21] and $KF-Al_2O_3$, [22] have been reported. In addition, Ionic liquids [23] and solvent-free conditions [24] have also been reported.

Although, these approaches are satisfactory for the synthesis of pyrazoles, these methods suffer from

drawbacks, such as long reaction times, low product yields, the harsh reaction conditions, expensive reagents, requirement of the stoichiometric amounts of catalysts, formation of a large amount of waste and/ or use of toxic organic solvents.

Although a number of different methods have been reported for the preparation of pyrazoles, there is still a need to search for better catalysts with regards to their handling and economic viability.

In the recent years, the use of nano-structured ZnO [25], nano-sulfated zirconia [26], nano- γ -alumina [27], and nano-ZSM-5 zeolite [28] catalysts has received considerable interest in organic synthesis. This extensive application of heterogeneous catalysts in synthetic organic chemistry can make the synthetic process more efficient from both environmental and economic point of view [29] and used-catalyst can be easily recycled.

As a part of our continuing effort towards the development of useful synthetic methodologies [30], here in we report an efficient process for synthesis of various pyrazoles, in the reaction of different 1,3-dicarbonyl compounds with hydrazines/hydrazides using nano-structured ZnO, nano-sulfated zirconia, nano- γ -alumina and nano-ZSM-5 zeolites, as the catalyst.

* Corresponding author: E-mail: a_teimouri@pnu.ac.ir

2. Experimental

2.1. Instruments and characterization

All reagents were purchased from Merck and Aldrich and used without further purification. Products were characterized by spectroscopy data (IR, FTIR, ^1H NMR and ^{13}C NMR spectra), elemental analysis (CHN) and melting points. A JASCO FT/IR-680 PLUS spectrometer was used to record IR spectra using KBr pellets. NMR spectra were recorded on a Bruker 400 Ultrasheild NMR and DMSO- d_6 was used as solvent. Melting points reported were determined by open capillary method using a Galen Kamp melting point apparatus and are uncorrected. Mass Spectra were recorded on a Shimadzu Gas Chromatograph Mass Spectrometer GCMS-QP5050A/Q P5000 apparatus.

2.2. Synthesis of Nano-crystalline sulfated zirconia

Nano-crystalline sulfated zirconia has been prepared by one step sol-gel technique [31]. A typical synthesis involves the addition of concentrated sulfuric acid (1.02 ml) to zirconium n-propoxide precursor (30 wt%) followed by the hydrolysis with water. After 3 h retain at room temperature, the resulting gel was dried at 110 °C for 12 h followed by calcination at 600 °C for 2 h.

2.3. Synthesis of nano-structured ZnO

Nano-structured ZnO has been prepared by one step sol-gel technique [32]. In a typical procedure, mixtures of ethanol, diethanolamine (DEA) and zinc acetate dihydrate, were prepared. The concentration of zinc acetate dihydrate in solvent was 0.2 M. The molar ratio of zinc acetate and diethanolamine was 1.0 and the pH of the mixture was reached to about 9. When the zinc acetate crystals were dissolved completely, sodium hydroxide (NaOH) pellets were added to the solution to increase the pH of the mixture to about 11. The resultant solution was then transferred into the stainless steel autoclave which was sealed and maintained at 130 °C for 24 h.

2.4. Synthesis of nano- γ - Al_2O_3 catalyst

The nano- γ - Al_2O_3 was prepared by sol-gel method according to a procedure described [27]. In a typical experiment, Aluminum nitrate (15.614 g) was added to 400 ml of deionized water. Similarly, solution of sodium carbonate is prepared by dissolving (7.95 g) in 400 ml of deionized water. 200 mL of deionized water is taken in a 2 l capacity round-bottom flask and stirred well using magnetic stirrer. Then sodium carbonate and aluminum nitrate solutions are added to 200 ml of deionized water (from separate burettes) drop wise.

The temperature was maintained at 70 °C during experiment. The pH after precipitation was found to be in the range of 7.5–8.5. The mixture was stirred for 4 h. The digested precipitates were filtered and re-dispersed

again in hot 2 l of deionized water, filtered and finally washed with ethanol first followed by acetone to avoid contamination of 'Na⁺' ions; and air dried at room temperature. The dried precipitates were calcined in a furnace at 550 °C for 5 h to produce nano-sized γ - Al_2O_3 powders.

2.5. Synthesis of nano-ZSM-5

For synthesis of nano-ZSM-5, tetrapropyl ammonium hydroxide and tetra ethyl ortho silicate were the sources of aluminum and silicon, respectively. Nano-ZSM-5 Zeolite was synthesized according to the procedure described earlier [33]. The components were mixed with constant stirring. After adding all the ingredients, the solution was left to hydrolyze at room temperature for 48 h. The obtained gel was heated at 80 °C to evaporate water and ethanol formed during the reaction. The obtained solution was charged into the stainless-steel autoclave under pressure and static conditions at 170 °C for of 48 h. The solid phase obtained was filtered, washed with distilled water several times, dried at 120 °C and then calcined at 550 °C for 12 hours.

2.6. General procedure for the synthesis of pyrazole derivatives

A mixture of 1,3-dicarbonyl compound (1 mmol), hydrazine/hydrazide (1 mmol), were added in ethanol and stirred at r.t. The catalyst was added to the reaction mixture and the reaction was monitored by TLC. After the reaction was complete, EtOAc (2×20 mL) was added to the reaction mixture and the catalyst was separated by filtration. The organic solvent was removed under reduced pressure. Obtained products were further purified by chromatography on silica gel (ethyl acetate/n-hexane 30:70) as an eluent. Compounds were characterized by spectral data.

Selected spectral data:

3,5-Dimethyl-1-phenyl-1H-pyrazole (1a): b.p.= 252 °C; FTIR (film): $\bar{\nu}$ = 1681, 1595 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 2.28 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 5.97 (s, 1H, CH), 7.30-7.45 (m, 5H, C_6H_5); MS: m/z= 172.13; (M^+).

3,5-Dimethylpyrazole (1b): m.p.= 108 °C; FTIR (film): $\bar{\nu}$ = 3106, 1661, 1593 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 1.46 (t, 3H, CH_3), 2.27 (s, 3H, CH_3), 5.79 (s, 1H, CH), 10.66 (br s, 1H, N-H); MS: m/z= 96.14 (M^+).

5-Ethoxy-3-methyl-1-phenyl-1H-pyrazole (1c): FTIR (film): $\bar{\nu}$ = 1700, 1635, 1187 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 1.44 (t, 3H, CH_3), 2.26 (s, 3H, CH_3), 4.15 (q, 2H, CH_2), 6.15 (s, 1H, CH), 7.20-7.73 (m, 5H, C_6H_5); MS: m/z= 202.04 (M^+).

5-Ethoxy-3-methyl-1H-pyrazole (1d): m.p.= 120 °C; FTIR (film): $\bar{\nu}$ = 3004, 1690, 1592, 1161 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 1.42 (t, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.98 (q, 2H, CH_2), 5.91 (s, 1H, CH), 10.68 (brs, 1H, N-H); MS: m/z = 126.09 (M^+). Anal. Calcd for $\text{C}_6\text{H}_{10}\text{N}_2\text{O}$: C, 57.12; H, 7.99; N, 22.21. Found C, 56.95; H, 7.87; N, 22.28.

3,5-Diethoxy-1-phenyl-1H-pyrazole (1e): FTIR (film): $\bar{\nu}$ = 1670, 1562, 1357; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 1.61 (t, 3H, CH_3), 1.91 (t, 3H, CH_3), 4.25 (q, 2H, CH_2), 4.43 (q, 2H, CH_2), 5.93 (s, 1H, CH), 7.50-7.70 (m, 5H, C_6H_5); MS: m/z = 232.02 (M^+).

2.5.6. 3,5-Diethoxy-1H-pyrazole (1f): m.p.: 134-137 °C; FTIR (film): $\bar{\nu}$ = 1662, 1565, 1343 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 1.52 (t, 3H, CH_3), 1.91 (t, 3H, CH_3), 4.23 (q, 2H, CH_2), 4.33 (q, 2H, CH_2), 6.50 (s, 1H, CH); 10.63 (brs, 1H, N-H); MS: m/z = 156.01 (M^+). Anal. Calcd for $\text{C}_7\text{H}_{12}\text{N}_2\text{O}_2$: C, 53.83; H, 7.74; N, 17.94. Found C, 53.71; H, 7.58; N, 17.83.

3. Results and Discussion

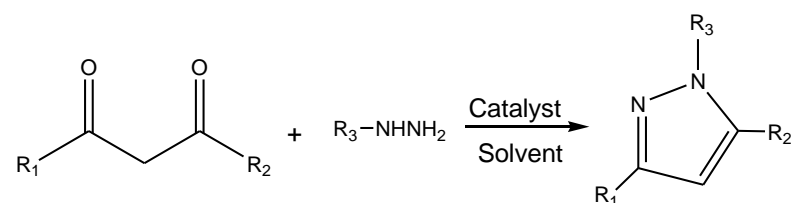
The results of pyrazoles synthesis from 1,3-dicarbonyl compounds with hydrazines/hydrazides under nano-structured ZnO, nano-sulfated zirconia, nano- γ -alumina and nano-ZSM-5 zeolites, as the catalyst has been shown in Table 1. The results showed that nano-crystalline sulfated zirconia (SZ) promoted the reaction more effectively than nano-structured ZnO, nano- γ -alumina and nano-ZSM-5 zeolites as far as the amount of catalyst and reaction time are concerned (Table 1). In conclusion, nano-crystalline sulfated zirconia (SZ)

was an effective catalyst for the reaction between 1,3-dicarbonyl compounds with hydrazines/hydrazides.

In a systematic study (Table 2), phenylhydrazine was added to a solution of acetylacetone and catalyst in ethanol and the reaction mixture was stirred at r.t. In an initial endeavor, a blank reaction was carried out using 1.0 equiv. acetylacetone, 1.0 equiv. and phenylhydrazine, in the presence of catalyst. The reaction was stirred in ethanol, even after 24 h, 10% of the expected product was obtained in the absence of catalyst. To further improve the yield and to optimize the reaction conditions, the same reaction was carried out in the presence of (10 mol %) of catalyst under similar conditions. A significant improvement was observed and the yield of product was dramatically increased up to 90% after stirring the mixture for only 5 h.

To minimize the formation of byproducts and to achieve good yield of the desired product, the reaction is optimized by varying the amount of catalyst (5, 10 and 15 mol%), An increase in the amount of nano SZ from 5 to 15 mol % increased the yield of the desired product to a great extent (85–90%, Table 3, entries 2-4). The percentage yield of the product with 5, 10 and 15 mol% of nano-ZnO as a catalyst are 70%, 75% and 65%, respectively (Table 3, entries 5-7). For the nano-ZMS-5 and nano- γ -alumina as the catalyst, when the catalyst content was increased to 15 mol %, the product yield decreased to 70% (Table 3, entry 10) and 60% (Table 3, entry 13) respectively. Therefore, it was found that the use of 10 mol % of the catalyst was sufficient to promote the reaction, and greater amounts of the catalyst did not improve the yields.

Table 1. Acid-catalyzed synthesis of pyrazole derivatives.^a



Entry	Product	R ₁	R ₂	R ₃	Time (h) /Yield (%) ^b	m.p. (°C)	m.p. Lit. (°C)	Ref.
1	1a	CH ₃	CH ₃	Ph	5/85	Oil	-	-
2	1b	CH ₃	CH ₃	H	5/80	104-106	107	[18]
3	1c	CH ₃	OC ₂ H ₅	Ph	6/80	Oil	-	-
4	1d	CH ₃	OC ₂ H ₅	H	6/75	118-120	120	[16]
5	1e	OC ₂ H ₅	OC ₂ H ₅	Ph	6/78	Oil	-	-
6	1f	OC ₂ H ₅	OC ₂ H ₅	H	6/85	132-134	134-137	[16]

^a The products were characterized by IR, $^1\text{H-NMR}$, and mass spectroscopy.

^b Isolated yields.

Table 2. Reaction of acetylacetone with phenylhydrazine at r.t. in etanol catalyzed by different catalysts.

Entry	Catalyst	Catalyst (mol%)	Time (h)	Yield (%) ^a
1	None	-	24	No reaction
2	nano-SZ	5	5	85
3	nano-SZ	10	5	90
4	nano-SZ	15	5	75
5	nano-ZnO	5	5	70
6	nano-ZnO	10	5	75
7	nano-ZnO	15	5	65
8	nano- γ -alumina	5	5	75
9	nano- γ -alumina	10	5	80
10	nano- γ -alumina	15	5	70
11	nano-ZMS-5	5	5	65
12	nano-ZMS-5	10	5	70
13	nano-ZMS-5	15	5	60

^a Yields after isolation of products.

The effect of different solvents on reaction rate as well as yields of products was also investigated and the results are summarized in Table 3. Water, ethanol, methanol and acetonitrile provided excellent yields and proved to be the solvent of choice, whereas THF, 1,4-dioxane afforded lower yields.

One of the most important advantages of heterogeneous catalysis over the homogeneous counterpart is the possibility of reusing the catalyst by simple filtration, without loss of activity. The recovery and reusability of the catalyst was investigated in the

product formation. After completion of the reaction, the catalyst was separated by filtration, washed 3 times with 5 ml acetone, then with doubly distilled water several times and dried at 110 °C. Then the recovered catalyst was used in the next run.

X-ray diffraction pattern were recorded on diffractometer (Philips X'pert) using CuK α radiation ($\lambda=1.5405 \text{ \AA}$), angle range was between 0 and 80° (Figs. 1-2), Crystallite size of the crystalline phase was determined from the peak of maximum intensity ($2\theta=30.18$) by using Scherrer formula [34], with a

Table 3. Effect of solvent on the reaction times and yields.

Entry	Solvent ^a	Time (h) ^b	Yield (%) ^c
1	H ₂ O	5	85
2	EtOH	5	90
3	MeOH	5	80
4	CH ₃ CN	5	75
5	1,4-Dioxan	5	70
6	THF	5	60

^a Reaction was performed with acetylacetone (1 mmol) and phenylhydrazine (1 mmol) in the presence of catalyst in various solvents.

^b Reaction time monitored by TLC.

^c Isolated yield.

Table 4. Comparison of the efficiency of nano-crystalline SZ with other reported catalysts in the synthesis of pyrazole derivatives^a.

Entry	Catalyst (mol %)	Conditions	Time (h)	Yield (%) ^a	Ref.
1	nano-crystalline SZ	EtOH/Reflux	5	90	This work
2	Zn[(L)proline] ₂	EtOH/r.t	6	90	[16]
3	Amberlyst-70	H ₂ O/r.t	0.5	89	[12]

^a Reaction was performed with acetylacetone (1 mmol) and phenylhydrazine (1 mmol) in the presence of catalyst.

shape factor (K) using Scherrer formula [34], with a shape factor (K) of 0.9, as below: Crystallite size = $K\lambda/W\cos\theta$, where, $W=W_b-W_s$ and W_b is the broadened profile width of experimental sample and W_s is the standard profile width of reference silicon sample. FT-IR spectra of the catalysts were recorded by FT-IR spectrophotometer in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} by mixing the sample with KBr (Figs. 3,4).

Specific surface area, pore volume and pore size distribution of sulfated zirconia samples calcined at

600 °C were determined from N₂ adsorption–desorption isotherms at 77K (ASAP 2010 Micromeritics). Surface area was calculated by using BET equation; pore volume and pore size distribution were calculated by BJH method [35].

The samples were degassed under vacuum at 120 °C for 4 h, prior to adsorption measurement to evacuate the physisorbed moisture. The detailed imaging information about the morphology and surface texture of the catalyst was provided by SEM (Philips XL30 ESEM TMP), (Fig. 5).

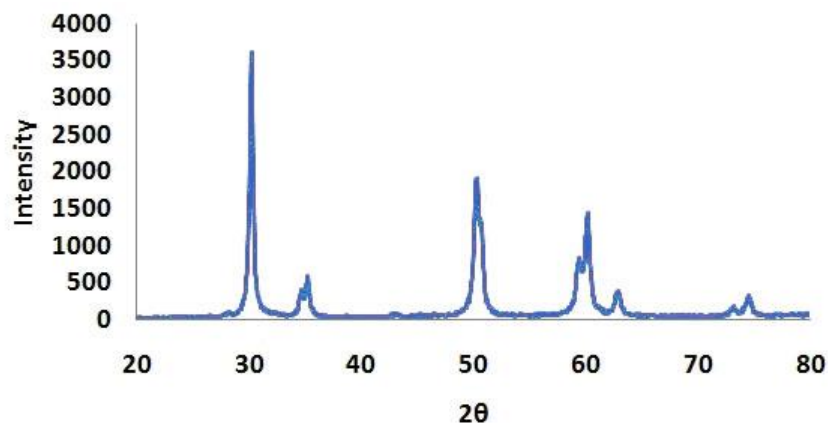


Fig 1. XRD pattern of nano-sulfated-zirconia catalyst.

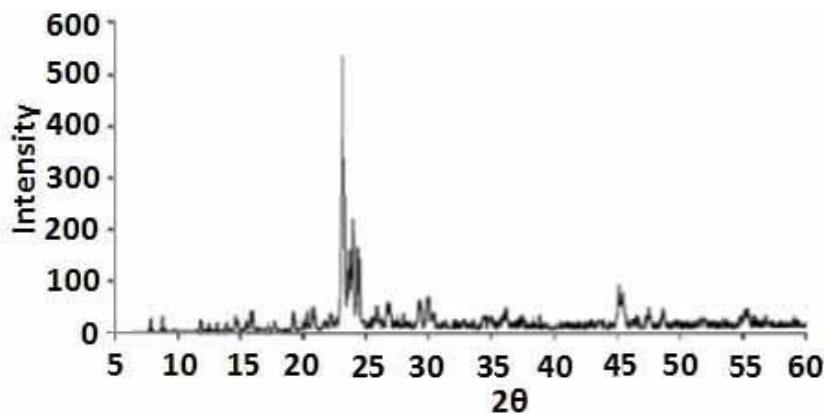


Fig 2. XRD pattern of nano-ZSM-5 catalyst.

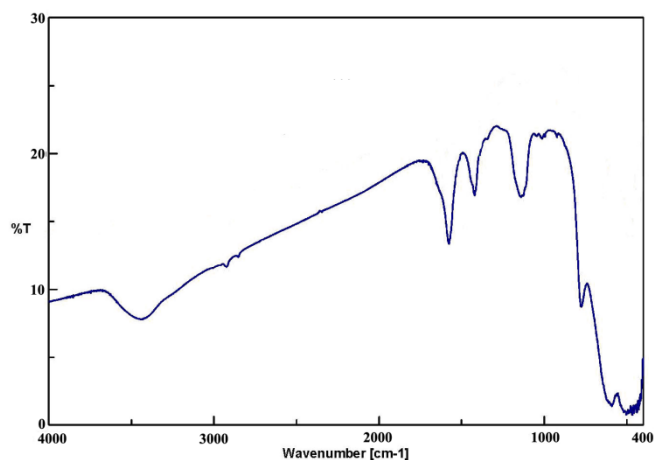


Fig 3. FT-IR spectra nano-sulfated-zirconia catalyst.

The XRD patterns of sulfated-zirconia and ZSM-5 powders obtained. Characteristic peaks of sulfated-zirconia appeared at 30.18, 34.61°, 35.28°, 50.21°, 50.77°, 59.29°, 60.18°, 62.72°, 72.89° and 74.617. (Fig. 1) Characteristic peaks of ZSM-5 appeared at the region of $2\theta=22.5-25$ (Fig. 2).

The FT-IR spectra of sulfated-zirconia (Fig. 3) showed a broad peak at around 3400 cm^{-1} is attributed to the O-H stretching mode of water related with zirconia. An intense peak around 1630 cm^{-1} is attributed to O-H bending mode of water associated with the sulfate group.

The FT-IR spectra of this catalyst showed band around $900-1200\text{ cm}^{-1}$, these are assigned to SO_4^{2-} modes. A middle peak at approximately 1500 cm^{-1} is observed in the spectra assigned to asymmetric stretching of covalent S=O band and a peak at about 750 cm^{-1} is formed which assign to typical bands of Zr-O.

The FT-IR spectra of alumina samples calcined at 550°C (Fig. 4) showed an intense band centered around 3500 cm^{-1} and a broad band at 1650 cm^{-1} , these are assigned to stretching and bending modes of adsorbed water. The Al-O-Al bending stretching vibrations observed at around 1150 cm^{-1} are due to symmetric and asymmetric bending modes, respectively.

The OH torsional mode observed at 800 cm^{-1} overlaps with Al-O stretching vibrations. The weak band at 2091 cm^{-1} is assigned to a combination band. The bands observed at 617 and 481 cm^{-1} are attributable to stretching and bending modes of AlO_6 .

The morphology of the as prepared sulfated-zirconia powders analyzed by SEM is shown in Fig. 5. The SEM image demonstrates clearly the sulfated-zirconia powders indicated strong agglomeration of particles with varied spherical sizes.

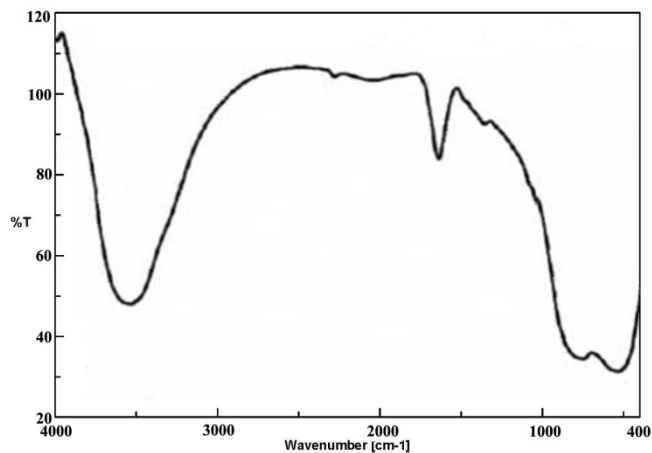


Fig 4. FT-IR spectra nano- γ -alumina catalyst.

4. Conclusions

In conclusion, we have demonstrated an efficient, versatile and convenient method for the synthesis of pyrazoles derivatives in reaction of different 1,3-dicarbonyl compounds with hydrazines/hydrazides. A comparison of the catalytic efficiency of nano-sulfated zirconia, nano-structured ZnO, nano- γ -alumina and nano-ZSM-5 zeolites with the nano-sulfated zirconia exhibiting greater activity has also been demonstrated. Compared to previously reported methods, the mild reaction conditions, high yields, easy work-up, clean reaction profiles and lower catalyst loading render this approach as an interesting alternative to the existing methods.

Acknowledgement

Supports from the Payame Noor University in Isfahan research council and helps of Isfahan University of Technology are gratefully acknowledged.

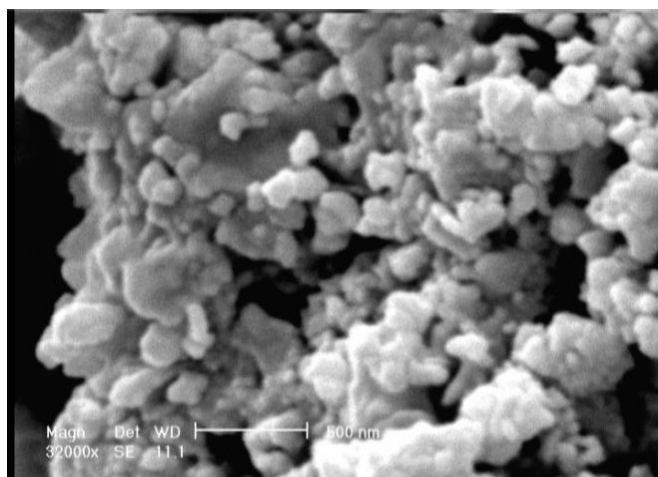


Fig 5. SEM micrograph of nano-sulfated-zirconia catalyst.

References

- [1] L.C. Behr, R. Fusco, C.H. Jarboe, in: R.H. Wiley (Ed.), *Pyrazoles, Pyrazolines, Pyrazolidines, Indazoles and Condensed Rings*, Inter-Science, New York, 1967.
- [2] J. Elguero, in: A.R. Katritzky, C.W. Rees, E.F. Seriven (Eds.), *Comprehensive Heterocyclic Chemistry II*, vol. 3, Pergamon, Oxford, 1996, p. 1.
- [3] R.N. Mahajan, F.H. Havaladar, P.S. Fernandes, *J. Indian Chem. Soc.*, 68 (1991) 245-249.
- [4] S.L. Janus, A.Z. Mafdif, B.P. Erik, N. Claus, *Monatsh. Chem.*, 130 (1999) 1167-1174.
- [5] A.R. Katritzky, A.V. Vakulenko, R. Akue-Gedu, A.V. Gromova, R. Witek, J.W. Rogers, *Arkivoc*, (2007) (i) 9-21.
- [6] Z. Wang, H. Qin, *Green Chem.*, 6 (2004) 90-92.
- [7] A.R. Katritzky, *Handbook of Heterocyclic Chemistry*. Pergamon, New York, 1985, p. 416.
- [8] V.K. Aggarwal, J. De Vicente, R.V. Bonnert, *J. Org. Chem.*, 68 (2003) 5381-5383.
- [9] B.A. Bhat, S.C. Puri, M.A. Qurishi, K.L. Dhar, G.N. Qazi, *Synth. Commun.*, 35 (2005) 1135-1142.
- [10] B.C. Bishop, M.J. Kaul Brand, D.A. Gibb, J.D. Kennedy, *Synthesis*, 1 (2004) 43-52.
- [11] M.S.M. Ahmed, K. Kobayashi, A. Mori, *Org. Lett.*, 7 (2005) 4487-4489.
- [12] H.S. Chandak, N.P. Lad, D.S. Dange, *Green Chem. Lett. Rev.*, (2011) 1-4.
- [13] V. Polsheettiwar, S.R. Varma, *Tetrahedron Lett.*, 49 (2008) 397-400.
- [14] J. Velasco, E. Pérez-Mayoral, G. Mata, M. Luisa Rojas-Cervantes, M.A. Vicente-Rodríguez, *Appl. Clay Sci.*, 54 (2011) 125-136.
- [15] C.T. Eary, D. Clausen, *Tetrahedron Lett.*, 47 (2006) 6899-6902.
- [16] M. Kidwai, A. Jain, R. Poddar, *J. Organomet. Chem.*, 696 (2011) 1939-1944.
- [17] F. Texier-Boullet, B. Klein, J. Hamelin, *Synth. Commun.*, (1986) 409-411.
- [18] Xiang Chen, Jin She, Zhicai Shang, Jun Wu, Haifeng Wu, Peizhi Zhang, *Synthesis*, 21 (2008) 3478-3486.
- [19] M. Curini, O. Rosati, V. Campagna, F. Montanari, G. Cravatto, M. Boclini, *Synlett*, 19 (2005) 2927-2930.
- [20] S. Hayat, Atta-ur-Rahman, M.I. Choudhary, K.M. Khan, W. Schumann, E. Bayer, *Tetrahedron*, 57 (2001) 9951-9957.
- [21] M.W. Branco, R.Z. Cao, L.Z. Liu, G. Ege, *J. Chem. Res.*, (1999) 274-275.
- [22] F.M. Moghaddank, S.M. DokhTaimooryk, H. Ismaili, G.R. Bardajeek, *Synth. Commun.*, 36 (2006) 3599-3607.
- [23] C.P. Frizzo, D. N. Moreira, E.A. Guarda, G. F. Fiss, M.R.B. Marzari, N. Zanatta, H.G. Bonacorso, M. A.P. Martins, *Catal. Commun.*, 10 (2009) 1153-1156.
- [24] J.S. Yadav, B.V.S. Reddy, G. Satheesh, P. Naga Lakshmi, S. Kiran Kumar. A. C. Kunwar, *Tetrahedron Lett.*, 45 (2004) 8587-8590.
- [25] S. Khameneh Asl, S.K. Sadrnezhad, M. Kianpour rad, *Mater. Lett.*, 64 (2010) 1935-1938.
- [26] V. Indovina, D. Pietrogiamomi, M.C. Campa, *Appl. Catal. B*, 39 (2002) 115-124.
- [27] H.S. Potdar, K.W. Jun, J.W. Bae, S.M. Kim, Y.J. Lee, *Appl. Catal.*, A 321 (2007) 109-116.
- [28] Y. Ni, A. Sun, X. Wu, G. Hai, J. Hu, T. Li, G. Li, *Microporous Mesoporous Mater.*, 143 (2011) 435-442.
- [29] G. Santor, R. Maryi, P. Righi, *Chem. Ber.*, 104 (2004) 199.
- [30] A. Teimouri, A. Najafi Chermahini, *J. Mol. Catal. A: Chemical*, 346 (2011) 45-39.
- [31] B. Tyagi, M.K. Mishra, R.V. Jasra, *Catal. Commun.*, 7 (2006) 52-57.