Full paper

Applied
Organometallic
Chemistry

Received: 17 May 2015 Revised: 2 July 2015 Accepted: 8 July 2015

(wileyonlinelibrary.com) DOI 10.1002/aoc.3358

Synthesis of 5-substituted 1*H*-tetrazoles using a recyclable heterogeneous nanonickel ferrite catalyst

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An efficient method was developed for the [2 + 3] cycloaddition of sodium azide with nitriles to afford 5-substituted 1*H*-tetrazoles using nanonickel ferrite ($NiFe_2O_4$) as an effective heterogeneous catalyst in dimethylformamide. The main advantages of this method are high yields, simple methodology and easy work-up. The catalyst can be recovered and reused for several cycles with predictable activity. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: heterogeneous catalyst; nickel ferrite nanoparticles; cycloaddition; 5-substituted 1*H*-tetrazoles

Introduction

Tetrazoles are synthetic nitrogen-rich compounds with a wide range of applications that are receiving considerable attention among the stable heterocycles.[1] They play important roles in coordination chemistry,[2] in the photographic industry[3] and in the formation of photoinducible bioorthogonal ligations for the selective covalent attachment of synthetic groups to biopolymers such as proteins.[4] Furthermore, extensive work has been accomplished in the field of medicinal chemistry.[5] They are used for their biological activities such as antibacterial, anti-inflammatory, antifungal, antiviral, antituberculous, cyclo-oxygenase inhibitory, antinociceptive, hypoglycaemic and anticancer activities.[6] Tetrazole moieties are also important synthons in synthetic organic chemistry. For example, a proline-derived tetrazole is used as an enantioselective catalyst in asymmetric synthesis and multicomponent reactions.[7] As a result of their acidities, 5-monosubstituted tetrazoles are also used as activators in oligonucleotide synthesis.[8]

Conventional synthesis of 5-substituted 1*H*-tetrazoles is via [2 + 3] cycloaddition of azides to the corresponding nitriles, first reported by Hantzsch and Vagt.[9] Various synthetic approaches have been developed for this transformation. Most of them depend on the *in situ* production of highly toxic, explosive, water-sensitive and volatile hydrazoic acid through activation of the azide by expensive and toxic metal organic azide complexes such as those of tin or silicon, strong Lewis acids or amine salts.[10] Later, a dramatic procedure involving stoichiometric amounts of Zn(II) salts was reported under reflux in H_2O.[11] Other recent developments include the synthesis of 5-substituted 1*H*-tetrazoles under solvent-free conditions,[12] and the use of various catalysts such as Cu_2O,[13] $BF_3{\cdot}OEt_2$,[14] $Pd(OAc)_2/ZnBr_2$,[11] $Yb(OTf)_3$,[15] $Zn(OTf)_3$,[16] $AlCl_3$,[17] $CuSO_4$,[18] $Pd(PPh_3)_4$,[19] $TMSN_3$/TABF[12] and boron azides.[20] However, a drawback of these homogeneous catalytic processes is the difficulty in separation and recovery of the catalysts. Therefore, many researchers have developed various heterogeneous catalyst systems, such as silica-supported $FeCl_3$,[21] ZnS nanospheres,[22] Cu–Zn alloy nanopowder,[23] Zn/Al hydrotalcite,[24] Sb_2O_3,[25] zinc hydroxyapatite,[26] $CdCl_2$,[27] metal tungstates,[28] γ-Fe_2O_3,[29] natural natrolite zeolite,[30] nano-ZnO/Co_2O_3,[31] CoY zeolite,[7] $CuFe_2O_4$ nanoparticles,[32] zeo-lite/sulfated zirconia,[33] phosphomolybdic acid,[34] amberlyst-15[35] and $Ln(OTf)_3$-SiO_2.[36]

Herein, we report the synthesis of 5-substituted 1*H*-tetrazoles from various aryl/heteroaryl cyanides and sodium azide under conventional heating using nickel ferrite ($NiFe_2O_4$) nanoparticles as a recyclable catalyst. Nickel ferrite nanoparticles are one of the most important members of the spinel ferrites, a main category of bimetallic nanoparticles displaying very good catalytic activity in various organic reactions. Use of bimetallic nanoparticles as a catalyst leads to better selectivity and catalytic activity and higher deactivation resistance compared to monometallic ones.

Results and discussion

Nickel ferrite nanoparticles were prepared using a co-precipitation method according to the procedure presented by Aliahmad and Noori.[37] In the first step of the process, $Ni(OH)_2$ and $Fe(OH)_3$ are obtained with a higher reaction activity. When the solution is heated to 70°C, the metal hydroxides are decomposed to produce NiO and Fe_2O_3 in the reaction process (Scheme 1). Nickel ferrite nanoparticles are formed when the sample is calcined at 500°C for 3h.[38]

In order to characterize the catalyst structure, the synthesized nanoparticles were analysed using Fourier transform infrared (FT-IR) spectroscopy, X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

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$$NiCl_2 \cdot 6H_2O + 6NaOH \xrightarrow[-2NaCl,\ -6H_2O]{} Ni(OH)_2 \longrightarrow NiO + H_2O$$

$$2FeCl_3 \cdot 6H_2O + 6NaOH \xrightarrow[-6NaCl,\ -12H_2O]{} 2Fe(OH)_3 \longrightarrow Fe_2O_3 + 3H_2O$$

$$NiO + Fe_2O_3 \xrightarrow{500^oC} NiFe_2O_4$$

Scheme 1. Synthesis of nickel ferrite nanoparticles.

The FT-IR spectrum of nickel ferrite nanoparticles (Fig. 1) shows broad bands at 3438 and 1632 cm^{-1} assigned to OH stretching and bending modes of water, respectively. Intrinsic stretching vibration of the metal atom at the tetrahedral site, $M_{tetra}{\leftrightarrow}O$ (ν_1), is observed at 573 cm^{-1}, and the characteristic band at 401 cm^{-1} (ν_2) is attributed to octahedrally bonded metal atom stretching vibrations, $M_{octa}{\leftrightarrow}O$. The different frequencies of the characteristic vibrations (ν_1 and ν_2) may be attributed to the long bond length of oxygen–metals ions in the octahedral sites (Fe–O) and shorter bond length of oxygen–metals ions in the tetrahedral sites (Ni–O).[39]

The XRF results indicate that the amount of elemental Ni is 23.47%. This is in very good accordance with the formulation of the nickel ferrite structure, $NiFe_2O_4$.

The powder XRD pattern of the nickel ferrite nanoparticles is shown in Fig. 2. The diffraction peaks observed at $2\theta = 30.70°$, 36.02°, 37.6°, 43.92°, 54.28°, 57.77° and 63.4° correspond to the planes of (220), (311), (222), (400), (422), (511) and (440), respectively. The (311) peak has the highest intensity in the XRD pattern. All of the Bragg reflection peaks confirm the formation of $NiFe_2O_4$. No diffraction peaks of impurities such as α-Fe_2O_3 or NiO and other secondary phases are detected. It is clearly observed that the reflection peaks are sharp and narrow, indicating a high degree of crystallinity and phase purity of the product. The diffraction lines provide clear evidence for the formation of the cubic spinel structure of nickel ferrite with lattice parameter $\alpha = 8.34$ Å.

The surface morphology, orientation and particle sizes of the nickel ferrite nanoparticles were determined using SEM. The SEM images (Fig. 3) show a relatively uniform dispersion of nanoparticles with an average particle size of *ca* 10 nm.

After confirming the exact characteristics of the catalyst, the catalytic activity of the nanoparticles was examined in the synthesis of 5-substituted 1*H*-tetrazoles from various aryl/heteroaryl cyanides. In order to improve the efficiency of the reaction, the solvent was optimized at different temperatures and in the presence of various concentrations of catalyst. Initially, the reaction conditions were optimized for the reaction of 4-chlorobenzonitrile with sodium azide in the presence of various solvents using 5 mol% of catalyst (Table 1). Several organic solvents, namely tetrahydrofuran (THF), dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), dioxane and toluene, and also water as a green and non-toxic solvent were examined. According to the data in Table 1, DMF is the most efficient solvent for this reaction (Table 1, entry 9).

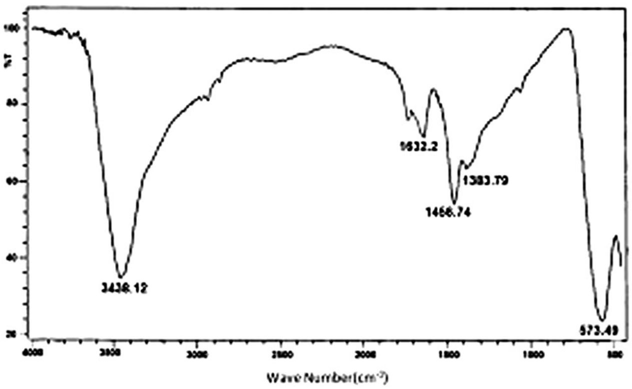


Figure 1. FT-IR spectrum of $NiFe_2O_4$ nanoparticles synthesized using a co-precipitation method.

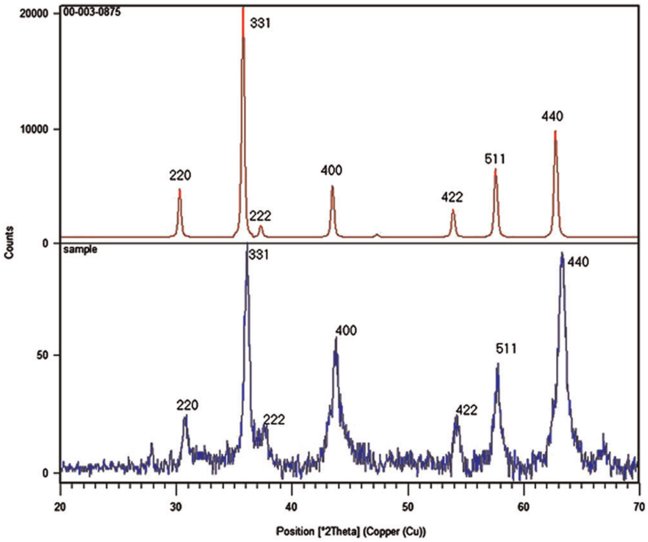


Figure 2. XRD pattern of nickel ferrite nanoparticles.

To study the effects of temperature, the reaction was initially carried out at room temperature and then at each of 50, 80, 100 and 120°C (Table 1, entries 6–10). It is evident from Table 1 that the yield of the reaction is considerably enhanced at 100°C. The yield remains almost constant at higher temperature.

Determination of the amount of catalyst required for the reaction is the next step. For this purpose, the reaction was carried out in the absence of the catalyst and also in the presence of 2, 5 and 10 mol% of the nanonickel ferrite catalyst under the obtained optimized reaction conditions: 5 mol% gives the best results (Table 1, entries 9 and 11–13). The reaction was evaluated in the absence of ammonium acetate. A longer time is required for the reaction to complete under this condition (Table 1, entry 14).

With these optimized reaction conditions in hand, the generality of this catalytic system for the synthesis of 5-substituted 1*H*-tetrazoles from various aryl/heteroaryl cyanides was explored. As evident from Table 2, reactions of *m*- and *p*-cyanopyridine with sodium azide afford nearly stoichiometric amounts of the products (Table 2, entries 3 and 4). The activity of nitrile compound towards azide ion plays an important role in this cycloaddition reaction. Among the various nitrile compounds, aromatic nitriles with electron-withdrawing substituents give higher yields in shorter reaction times (Table 2, entries 5, 8 and 12). However, when a nitrile bearing an electron-donating group is used as the reactant (Table 2, entries 6 and 7), the corresponding tetrazole is obtained in moderate to good yields with a prolonged reaction time. Malononitrile affords only mono-addition product even on addition of 2 equiv. of sodium azide (Table 2, entry 9).

1,4-Dicyanobenzene is an interesting substrate for study of mono-addition or di-addition reactions. It has been reported that the di-addition product is obtained using soluble Zn(II) salts as catalyst, whereas the mono-addition product is obtained with the use of solid zinc oxide catalyst. He and co-workers found that mono- and di-addition products could be selectively synthesized by simply adjusting the molar ratio of NaN_3 to nitriles and the rate of addition of NaN_3 to the reaction solution.[28] The di-addition

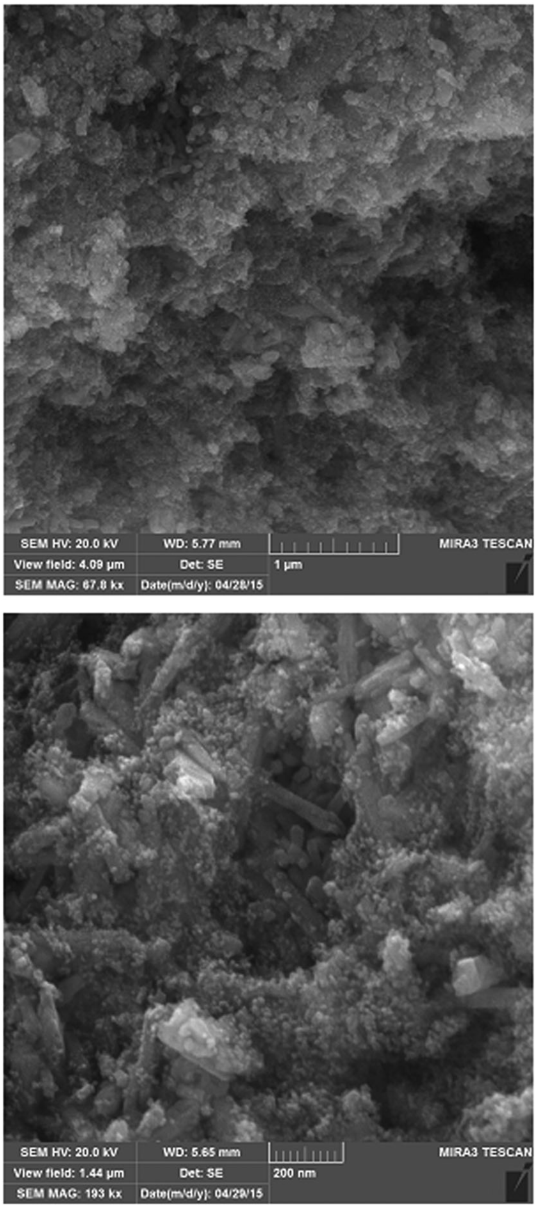
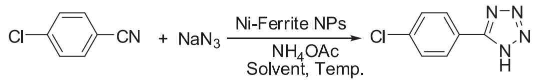


Figure 3. SEM images of synthesized nickel ferrite nanoparticles.

product was obtained when the molar ratio of NaN_3 to nitrile was about 2; whereas when the molar ratio was about 1, the methodology of adding NaN_3 to the reaction solution had a crucial influence on the formation of mono- and di-addition products. If NaN_3 is completely added into the reaction solution before the chemical reaction, both adducts are formed with similar yields (61:24). This indicates that the substrate and mono-addition products show similar reaction activity with NaN_3. On the other hand, if NaN_3 is added gradually over a period of 6 h, the dominant product is the mono-addition one.[29] It is noteworthy that 1,4-dicyanobenzene only gives mono-adduct even when using a 1:2 molar ratio of 1,4-dicyanobenzene to sodium azide and 10 mol% of $NiFe_2O_4$ (Table 2, entry 8).

The importance of a heterogeneous catalyst over its homogeneous counterpart is the ease of separation and reusability without loss of activity. The recovery and reusability of the catalyst were investigated in tetrazole formation under the optimized conditions. After completion of the reaction of 4-chloroben-zonitrile with sodium azide, the catalyst was separated from the reaction mixture with an external magnet, washed three times with 5 ml of acetone and then with doubly distilled water several times, and dried in an oven at 100°C for 3–4 h. This process assists in

Table 1. Optimization of reaction conditions for the synthesis of 5-(4-chlorophenyl)-1*H*-tetrazole under conventional heating conditions[a]



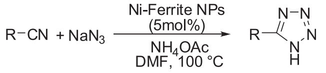
Entry	Solvent	Catalyst (mol%)	Temperature (°C)	Time (h)	Yield (%)[b]
1	THF	5	Reflux	2	10
2	DMSO	5	120	2	94
3	Dioxane	5	Reflux	2	8
4	Toluene	5	Reflux	2	20
5	H_2O	5	Reflux	7	30
6	DMF	5	Room temp.	2	60
7	DMF	5	50	2	75
8	DMF	5	80	2	80
9	DMF	5	100	2	98
10	DMF	5	120	2	98
11	DMF	—	100	4	0
12	DMF	2	100	2	44
13	DMF	10	100	2	98
14[c]	DMF	5	100	11	96

[a] Reactions conditions: 4-chlorobenzonitrile (1 mmol), NaN_3 (1.3 mmol), NH_4OAc (1 mmol), solvent (3 ml).

[b] Yield of isolated product.

[c] In the absence of ammonium acetate.

Table 2. Synthesis of 5-substituted 1*H*-tetrazoles catalysed by nickel ferrite nanoparticles (Ni-Ferrite NPs)[a]



Entry	R	Time (h)	Yield (%)[b]	M.p. (°C)[c]
1	C_6H_5-	3	94	215–217 (215–216)[7]
2	*p*-ClC_6H_4-	2	98	260–261 (261–263)[7]
3	3-Pyridinyl-	3	95	225–226 (224–225)[4]
4	4-Pyridinyl-	2	96	250–252 (251–253)[4]
5	*p*-FC_6H_4-	1	95	209–211 (210)[40]
6	*p*-$CH_3C_6H_4$-	3	90	247–249 (248–250)[40]
7	*o*-$NH_2C_6H_4$-	3	80	142–145 (143–144)[41]
8	*p*-CNC_6H_4-	2	98	257–258 (258–260)[33]
9[d]	$CNCH_2$-	1.5	96	115–117 (116–118)[7]
10	$C_6H_5CH_2$-	1	97	123–125 (123–124)[7]
11[e]	CH_3	1	94	146–147 (145–148)[7]
12	*p*-$NO_2C_6H_4$-	1	95	214–216 (215–217)[4]

[a] Reaction conditions: nitrile (1 mmol), sodium azide (1.3 mmol), ammonium acetate (1 mmol), catalyst (5 mol%), DMF (3 ml) at 100°C.

[b] Yield of isolated product.

[c] Literature values in parentheses.

[d] Reaction carried out in a pressure tube with 1.3 and 2.6 mmol of NaN_3.

[e] Reaction carried out in a pressure tube.

keeping the catalyst surface active. Then the recovered catalyst was used in the next run. It is noteworthy that the recycled catalyst retains optimum activity until the fourth cycle after which a drop in yield is observed (Fig. 4).

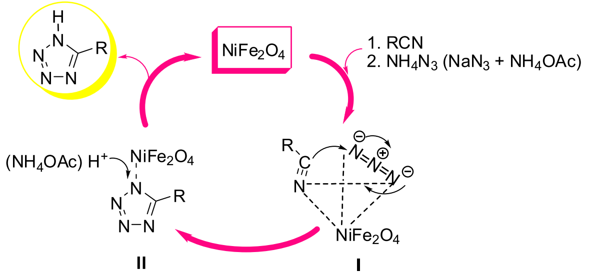
To evaluate the leaching phenomenon of the catalyst as a heterogeneous catalytic system, the reaction of 4-chlorobenzonitrile with sodium azide was repeated under optimized conditions in a defined time (1 h). However, for this bimetallic compound there is no support and the whole catalyst is a single spinel structure and therefore no leaching effect is observed in a formal form.[42] As evident from Table 2, this reaction completes in 2 h and it gives only 60% yield after 1 h. Then the catalyst nanoparticles were collected from the reaction mixture with an external magnet and the reaction was continued under the same conditions. After another 1 h, the reaction was stopped and its completion was again examined. The results show that the reaction in the absence of the catalyst no longer proceeds. This observation confirms that no leaching occurs in the reaction medium during the course of the reaction.

The efficiency of the catalyst was determined by comparison with other heterogeneous catalytic systems. It gives a better yield in shorter time (Table 3).

A plausible reaction pathway is proposed for the synthesis of 5-substituted 1*H*-tetrazoles using nickel ferrite nanoparticles as catalyst, as shown in Scheme 2. Initially, coordination of nitrogen atoms of nitrile and azide compounds with Ni(II) forms complex **I** which accelerates the cyclization step. This idea is supported by performing the reaction in the absence of $NiFe_2O_4$. Without any catalyst, cycloaddition reaction is not completed even after a long period of time (Table 1, entry 11). The [3 + 2] cycloaddition between the C≡N bond of nitrile compound and azide ion takes place readily to form the intermediate **II**. Protonolysis of intermediate **II** by H^+ of NH_4OAc or acidic extraction with HCl affords the 5-substituted 1*H*-tetrazole and $NiFe_2O_4$ catalyst. Ammonium acetate may produce ammonium azide *in situ* by reaction of ammonium acetate and sodium azide, increasing the availability of azide ion for [3 + 2] cycloaddition with nitrile, and also ammonium acetate is used as proton source to provide pure tetrazoles.[44,45]

Table 3. Comparison of various heterogeneous catalysts in 5-phenyl-1*H*-tetrazole formation

Entry	Catalyst	Temperature (°C)	Time (h)	Yield (%)	Ref.
1	CoY zeolite	120	14	90	7
2	Zn/Al hydrotalcite	120	12	84	24
3	$FeCl_3–SiO_2$	120	12	79	21
4	Nano-ZnO	120	14	72	43
5	Zinc hydroxyapatite	120	12	78	26
6	$CuWO_4·2H_2O$	120	24	72	29
7	$CuFe_2O_4$	120	12	82	32
8	Nanonickel ferrite	100	3	94	This work
9	γ-Fe_2O_3	120	36	81	30
10	Sulfated zirconia	120	24	90	33
11	Mesoporous ZnS nanospheres	120	36	96	22



Scheme 2. Plausible mechanism for the formation of tetrazoles.

Experimental

General

All melting points were determined in open capillaries with a Gallenkamp instrument. The FT-IR adsorption spectra were obtained with Nicolet 800 spectrophotometer using KBr discs. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker (Avance DRX-500) spectrometer at 500 and 125 MHz, respectively; using DMSO-d_6 as solvent at room temperature. Chemical shifts were reported in ppm relative to tetramethylsilane as an internal standard. XRD patterns of the catalyst were recorded with a PW 3710 X-ray diffractometer (Philips) at room temperature using monochromatic Cu Kα radiation with a wavelength of λ = 0.15418 nm. The peak position and intensity were obtained between 20° and 70° with a rate of 0.04° s^{-1}. The morphology of the catalyst was observed using a TSCAN SEM instrument.

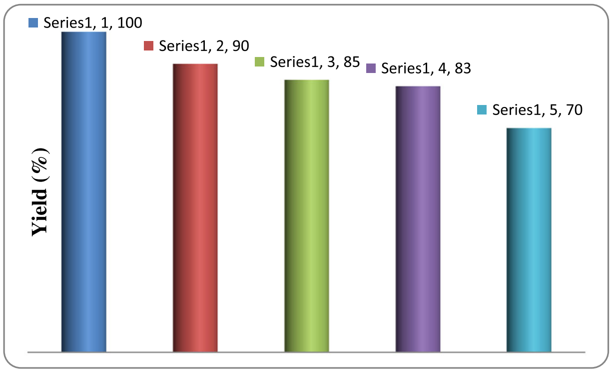


Figure 4. Recovery and reuse of nickel ferrite nanoparticles for the synthesis of 5-(4-chlorophenyl)-1*H*-tetrazole.

All reagents and solvents used in this study were commercially available and were purchased from commercial suppliers (Acros, Merck and Aldrich) and used without any additional purification.

Synthesis of nickel ferrite ($NiFe_2O_4$)

Solutions of iron chloride ($FeCl_3·6H_2O$) (0.2 M) and nickel chloride ($NiCl_2·6H_2O$) (0.1 M) were prepared separately and mixed together. In order for the pH to reach 13, a solution of NaOH (3 M) was added slowly to the flask. Finally, oleic acid (3 drops) was added to the solution as a surfactant and the suspension was vigorously stirred using a magnetic stirring bar at 70°C for 2 h. After complete precipitation, the residue was washed with double-distilled water (3 × 25 ml) and dried in an oven at 90°C overnight. It was then calcined at 500°C for 3 h.

General procedure for preparation of 5-substituted 1*H*-tetrazole

In a round-bottom flask equipped with a condenser for refluxing and a magnetic stirring bar, aryl/heteroaryl cyanide (1 mmol), sodium azide (1.3 mmol), ammonium acetate (1 mmol), nickel ferrite nanoparticles (5 mol%) and DMF (3 mL) were added and heated at 100°C under air atmosphere. The mixture was vigorously stirred under these reaction conditions and reaction completion was monitored using TLC (EtOAc–*n*-hexane, 75:25). After completion of the reaction, the catalyst was separated from the reaction mixture with an external magnet and the reaction mixture was treated with ethyl acetate (10 ml). The organic layer was treated with HCl (10 ml, 5 N) and stirred vigorously. The resultant organic layer was separated, and the aqueous layer was again extracted with ethyl acetate (10 ml). The combined organic layers were washed with water, dried over anhydrous magnesium sulfate and concentrated under reduced pressure using a rotary evaporator to give the crude solid crystalline 5-substituted 1*H*-tetrazole. The crude solid product was purified using silica gel column chromatography (EtOAc–*n*-hexane, 75:25).

All synthesized tetrazoles were characterized using spectral data (FT-IR, ^1H NMR and ^{13}C NMR) and melting points and comparing them with authentic samples.[4,7,33,40] The FT-IR spectra of synthesized compounds showed a sharp absorption at 3421 cm^{-1} (N–H), a group of bands at 1455 (C–H), 1285 (N–N=N–), 1208, 1120 and 1048 cm^{-1} caused by the presence of secondary amino group and tetrazole ring, and the absence of a band at 2200 cm^{-1} of the CN group. For example, the spectroscopic data for some products are presented in the following.

5-Phenyl-1*H*-tetrazole (Table 2, entry 1). White solid; m.p. 215–216°C. ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.12–7.59 (m, 2H, Ph), 7.53–7.51 (m, 3H, Ph), 3.92 (br, 1H, N–H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 154.8 (tetrazole ring), 131.2 (Ph), 130.0 (Ph), 127.1 (Ph), 124.2 (Ph). FT-IR (KBr, cm^{-1}): 3426, 3130, 3055, 2980, 2915, 2840, 2688, 2598, 1608, 1565, 1486, 1409, 1255, 1164, 1056, 991, 790, 725.

5-(4-Tolyl)tetrazole (Table 2, entry 6). White solid; m.p. 248–250°C. ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.93 (d, J = 9.0 Hz, 2H, Ph), 7.42 (d, J = 9.6 Hz, 2H, Ph), 3.35 (br, 1H, N–H), 2.4 (s, 3H, CH_3). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 155.0 (tetrazole ring), 139.2 (Ph), 130.0 (Ph), 126.8 (Ph), 121.6 (Ph), 21.3 (CH_3). FT-IR (KBr, cm^{-1}): 3413, 3095, 3067, 2964, 2909, 2850, 1610, 1488, 1435, 1259, 1159, 1093, 1017, 871, 804.

4-(1*H*-Tetrazole-5-yl)benzonitrile (Table 2, entry 8). White solid; m.p. 258–260°C. ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.21 (d, J = 9.9 Hz, 2H, Ph), 8.08 (d, J = 9.0 Hz, 2H, Ph). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 161.0 (tetrazole ring), 135.2 (Ph), 134.1 (Ph), 131.0 (Ph), 126.9 (CN), 115.3 (Ph). FT-IR (KBr, cm^{-1}): 3430, 3144, 3089, 3024, 2925, 2854, 2233, 1653, 1494, 1437, 1387, 1275, 1212, 1162, 1064, 995, 851, 746.

Conclusions

We report that nanonickel ferrite is an effective heterogeneous catalyst for the [2 + 3] cycloaddition of azide with a wide variety of nitriles to form 5-substituted 1*H*-tetrazoles with good to excellent yields. This catalyst can be separated and recovered easily from the reaction solution and can be reused for at least five consecutive runs without obvious loss in catalytic activity.

Acknowledgment

We gratefully acknowledge the funding support received for this project from Malek-ashtar University of Technology (MUT), Islamic Republic of Iran.

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