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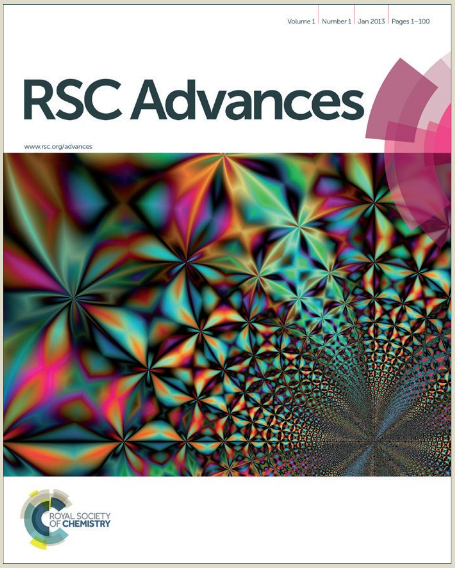

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Ni-S-methylisothiourea complex supported on boehmite nanoparticles and its application in the synthesis of 5-substituted tetrazoles

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Boehmite nanoparticles is an aluminum oxide hydroxide (ɤ-AlOOH) particles, which were prepared by simple and inexpensive procedure and immobilized further with nickel S-methylisothiourea complex (Ni-SMTU@boehmite), and characterized by FT-IR spectroscopy, TGA, XRD, ICP-OES, EDS, SEM and TEM techniques. Finally, we investigated the catalytic activity of Ni-SMTU@boehmite as a new, heterogeneous, stable and high reusable nanocatalyst for the synthesis of 5-substituted 1*H*-tetrazole derivatives in PEG-400 as green solvent. This catalyst was recovered by simple filtration and reused several times without significant loss of its catalytic efficiency or nickel leaching. Heterogeneity of this catalyst has been studied using hot filtration and ICP-OES technique.

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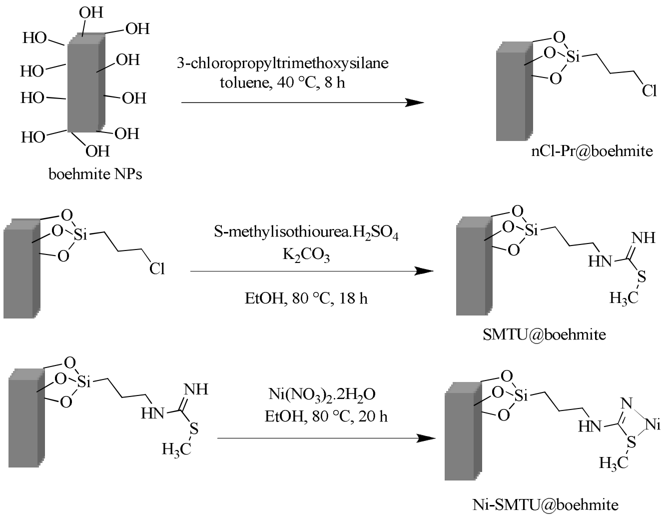
1 Introduction

Tetrazoles are an interesting class of nitrogen-rich heterocycles, also have wide range of applications as drugs in pharmaceuticals, in coordination chemistry as a ligand, in synthetic organic chemistry, in catalysis technology, in medicinal chemistry as stable surrogates for carboxylic acids, in the photographic industry, in organometallic chemistry as effective stabilizers of metallopeptide structures and in various materials science applications [1-6]. Recently tetrazole moieties were widely used for binding aryl thiotetrazolylacetanilides with HIV-1 reverse transcriptase [7]. Also, tetrazoles and their derivatives have been reported as analgesic, antiviral, anti-inflammatory, anti-proliferative, antibacterial, potential anti HIV drug candidate, antifungal, herbicidal and anticancer agents [8-12]. Valsartan and Losartan are two typical examples of the extensive application of these compounds as drugs, such as anti-hypertensive sartan family drugs [13]. Conventional synthesis of 5-substituted 1*H*-tetrazoles is [3 + 2] cycloaddition of azide to the corresponding nitriles. Recently, many catalysts have attracted increasing interest in the context for synthesis of tetrazole derivatives [1-12]. In order to combine the advantages of both homogeneous and heterogeneous catalysis, immobilization of homogeneous catalysts on heterogeneous nanomaterials have been widely used as efficient and reusable catalysts for synthesis of tetrazole derivatives [14]. However, many supports such as Zeolite [3, 12], MCM-41 [15], iron oxide [16], carbon nanotubes [17], graphene [18], heteropolyacids [19], ionic liquids [20] or some polymers [21] have been used as catalyst supports, which most of this supports are expensive or unstable. Also, synthesis of other nanoparticles requires inert atmosphere or high temperature for calcination or preparation [22-25]. While, boehmite nanoparticles is not air or moisture sensitive, more importance boehmite nanoparticles can be prepared in water at room temperature using available materials such as NaOH and $Al(NO_3)_3.9H_2O$ [25]. Boehmite is an aluminum oxide hydroxide (γ-AlOOH) particles including double sheets of octahedral with aluminum ions at their centers and the sheets themselves are composed of octahedral chains in cubic orthorhombic structure. The surface of boehmite nanoparticles are covered by many hydroxyl groups, which makes possible the modification of the surface of boehmite nanoparticles with other functional groups to supported catalysts such as metal complexes. Boehmite nanoparticles have several advantages such as non-toxicity, stability, high specific surface area (>120 m^2/g), ease of surface modification due to many hydroxyl groups on its surface, inexpensive and easily and readily availability [26-28]. Several methods such as sol–gel [29], hydrothermal [30] and hydrolysis of aluminum [31] have been reported for preparation of boehmite nanoparticles; but, most of them have focused on the effect of temperature, ultrasonic waves, time and Al/OH molar ratio on morphologies, chemical and physical properties of the prepared particles [33]. Also, Boehmite has been used as an optical material, absorbent, composite reinforcement material in ceramics, vaccine adjuvants, cosmetic products, coatings, starting material in the synthesis of alumina [32]. Meanwhile, nanoboehmite has been rarely used as support for catalyst [34-36]. Therefore herein a Nickel S-methylisothiourea complex immobilized on boehmite nanoparticles (Ni-SMTU@boehmite) has been reported as organometallic nanocatalyst for the synthesis of 5-substituted 1*H*-tetrazole derivatives using nitriles and sodium azide in PEG-400.

2 Results and discussion

2.1 Catalyst preparation

In order to prepare Ni-SMTU@boehmite, initially the boehmite nanoparticles was prepared according to new reported procedure [37], then modified using (3-chloropropyl)trimethoxysilane (CPTES). In the next step, the terminal Cl was successfully replaced by S-methylisothiourea hemisulfate salt (SMTU) through substation reaction, which SMTU has been supported on boehmite nanoparticles (SMTU@boehmite). Finally Nickel (II) particles have been coordinated with SMTU@boehmite (Scheme 1). The prepared catalyst has been characterized by FT-IR, XRD, TEM, SEM, EDS, TGA and ICP-OES analysis.



Scheme 1. Synthesis of Ni-SMTU@boehmite.

2.2 Catalyst characterizations

The XRD pattern of the boehmite nanoparticles, shows several peaks at *2Θ* values at 14.40 (0 2 0), 28.39 (1 2 0), 38.57 (0 3 1), 46.46 (1 3 1), 49.54 (0 5 1), 51.94 (2 0 0), 56.01 (1 5 1), 59.35 (0 8 0), 65.07 (2 3 1), 65.56 (0 0 2), 68.10 (1 7 1), and 72.38 (2 5 1) corresponded to crystal planes of boehmite nanoparticles in orthorhombic unit cell (Figure 1) [34, 35].

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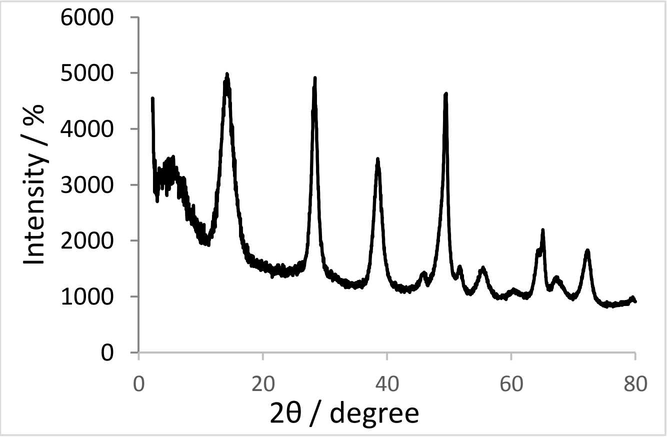
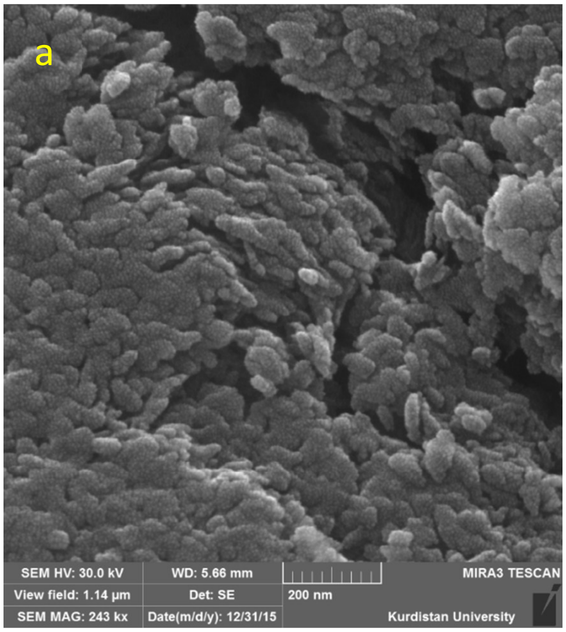


Figure 1. The XRD pattern of boehmite nanoparticles.

Scanning electron microscopy (SEM) was used to obtain direct information about the size and morphology of the prepared boehmite nanoparticles and Ni-SMTU@boehmite nanoparticles. SEM images show these nanoparticles was prepared with an average size about 20-40 nm (Figure 2), were of uniform size, and showed good dispersity. Also the size and morphology of Ni-SMTU@boehmite was studied by TEM technique. As shown in Figure 3, the unit cells of Ni-SMTU@boehmite was obtained in cubic orthorhombic structures with about 20-40 nm of size.



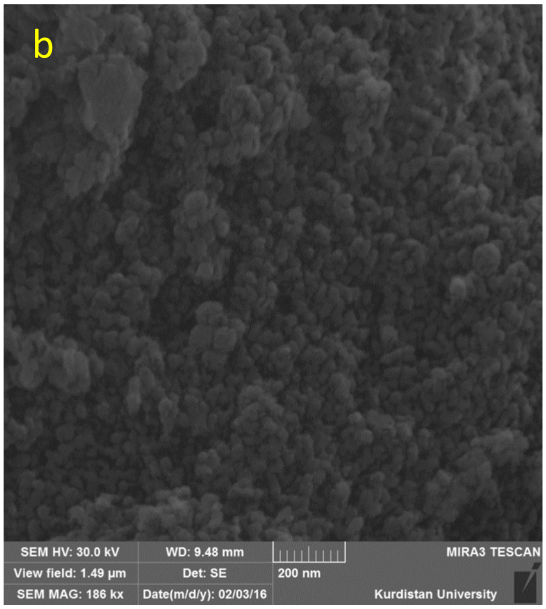
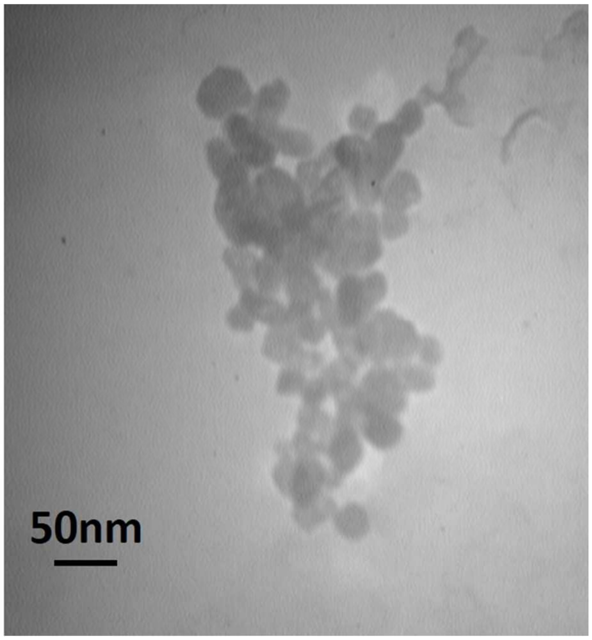


Figure 2. SEM images of boehmite nanoparticles (a) and Ni-SMTU@boehmite (b).



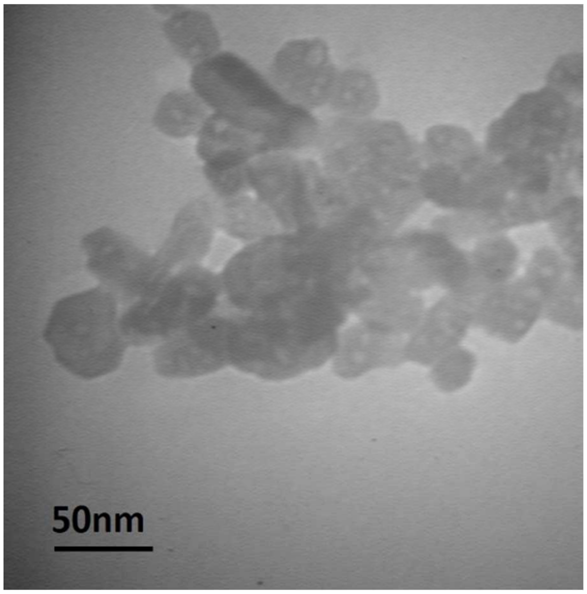


Figure 3. TEM images of Ni-SMTU@boehmite.

In order to show the presence elements in catalyst, the EDS analysis of Ni-SMTU@boehmite was performed. The EDS patterns of Ni-SMTU@boehmite is shown in Figure 4, that EDS spectrum of this catalyst indicates the presence of Al, O, Si, C, S and N and Ni specie in the catalyst.
Also, upon complexation of the modified boehmite nanoparticles with Ni, the exact amount of loaded metal was determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES). Based on ICP, the nickel content of described catalyst was 1.64×10^{-3} mol g^{-1}.

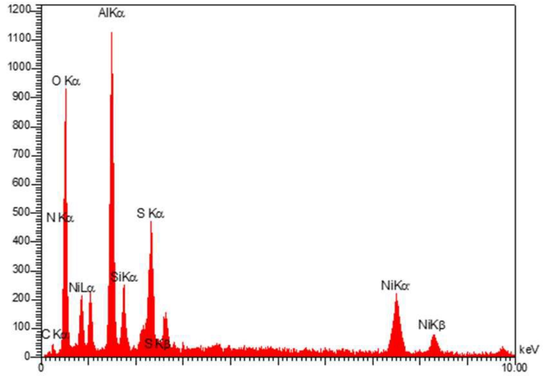


Figure 4. EDX spectrum of Ni-SMTU@boehmite.

Successful functionalization of Ni-complex on boehmite nanoparticles was confirmed by FT-IR technique (Figure 5). As shown in spectrum a, strong bands at 3086 and 3308 cm^{-1} are attributed to the symmetrical and asymmetrical modes of the hydroxyl groups on the surface of boehmite nanoparticles [37, 38]. In spectra a-d, several peaks at 480, 605 and 735 cm^{-1} are related to the Al-O bonds in boehmite structure [33]. Also, the nitrate impurity and hydrogen bands (OH…OH) vibration are appeared at (1637) and (1164 and 1069) cm^{-1} respectively [25, 32]. In spectrum b, the modification of boehmite nanoparticles with chloropropyltrimethoxysilane is authenticated by C–H stretching vibrations (2955 cm^{-1}) and O-Si stretching vibration (1073 cm^{-1}). In spectrum c, the existence of the grafted S-methylisothiourea groups has been proved by C=N vibration peak (1638 cm^{-1}) [38].

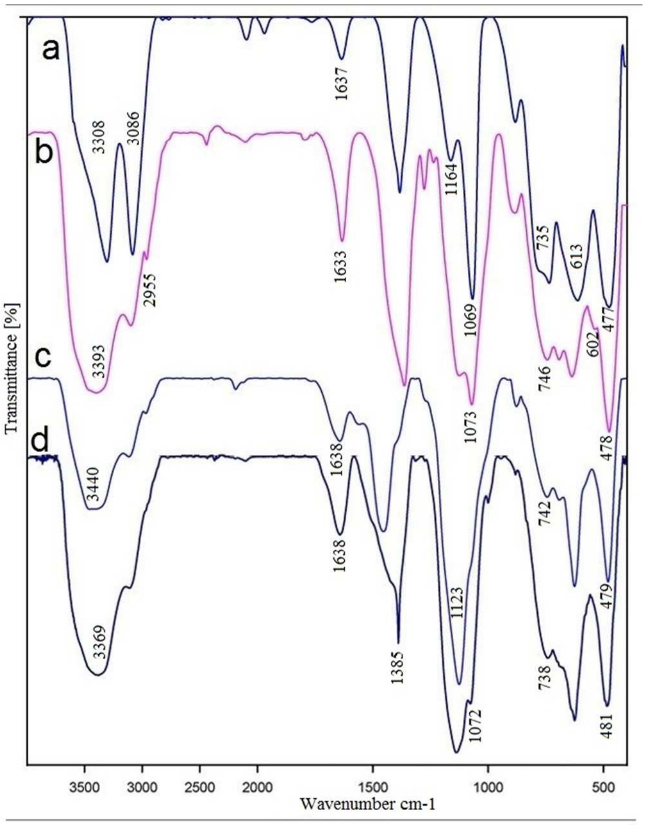


Figure 5. FT-IR spectra of boehmite nanoparticles (a), nCl-Pr@boehmite (b), SMTU@boehmite (c) and Ni-SMTU@boehmite (d).

In order to indicate the bond formation between the boehmite nanoparticles with the organic layers and Ni-complex, the TGA analysis was performed (Figure 6). The TGA curve of the Ni-SMTU@boehmite shows the mass loss of the supported complex and organic functional groups as it decompose upon heating. In the all samples, the negligible weight loss below 200 °C is due to the attached hydroxyl groups or adsorbed solvent molecules on the surface of nanoparticles [24]. But organic spacers and Ni-complex have been reported to desorb at temperatures above 260 °C. Based on TGA data, the weight losses of boehmite nanoparticles and SMTU@boehmite from 200 to 600 °C are 15% and 30%, respectively. While the weight loss of Ni-SMTU@boehmite is 47%. These results were confirmed that organic layers and Ni-complex have been anchored in the surface of boehmite nanoparticles.

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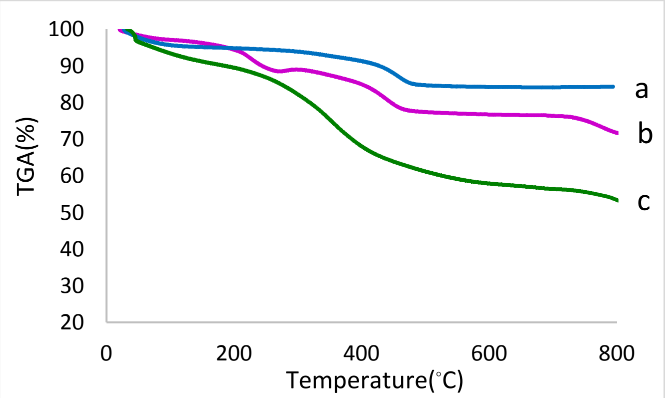
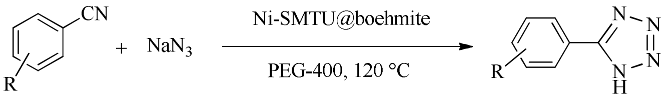


Figure 6. TGA diagram of boehmite nanoparticles (a), SMTU@boehmite (b) and Ni-SMTU@boehmite (c).

2.3 Catalytic study

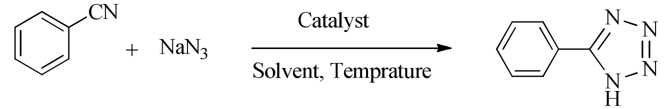
We examined the activity of Ni-SMTU@boehmite as an efficient, stable, reusable and commercially available catalyst for the synthesis of 5-substituted 1*H*-tetrazole derivatives.



Scheme 2. Synthesis of 5-substituted 1*H*-tetrazole derivatives in the presence of Ni-SMTU@boehmite.

In order to optimize the reaction conditions, the reaction of benzonitrile and sodium azide (NaN_3) was selected as a model reaction. The effect of various parameters such as temperature, solvents, amount of catalyst and NaN_3 were considered in the [2+3] cycloaddition reaction of benzonitrile with NaN_3 (Table 1). When, 15 mg of catalyst was used to catalyze the model reaction, the product was obtained in 52% yield within 80 min at 120 °C. Increasing the amount of catalyst from 20 to 25 mg was led to increasing in yield of product from 69 to 94%. While, increasing the amount of catalyst (from 25 to 30 mg) had no significant effect on yield of product. In order to find the best solvent for this transformation, the model reaction was studied in PEG-400, DMSO, DMF, H_2O and EtOH that the best results were obtained in PEG-400 (Table 1, entry 5). Also the effect of various amount of NaN_3 were examined in the [2+3] cycloaddition reaction of benzonitrile with NaN_3 (Table 1) and 1.4 mmol of NaN_3 was found to be for completion of reaction within 80 min at 120 °C (Table 1, entry 5). Also, we found that the reaction yields were susceptible to temperature changes. Therefore, the effect of temperature were described (Table 1, entries 10-12) and the best results were obtained at 120 ºC. As shown in Table 1, 0.025 g of Ni-SMTU@boehmite in PEG-400 at 120 °C using 1.4 mmol of NaN_3 was found to be ideal the reaction conditions for the synthesis of 5-substituted 1*H*-tetrazole derivatives.

Table 1. Optimization of reaction conditions for synthesis of 5-substituted 1*H*-tetrazole derivatives in the presence of Ni-SMTU@boehmite.



Entry	Catalyst (mg)	Solvent	NaN_3 (mmol)	Temperature (ºC)	Time (min)	Yield (%)[a]
1	30	PEG	1.2	120	80	60
2	30	PEG	1.3	120	80	73
3	30	PEG	1.4	120	80	93
4	25	PEG	1.4	120	80	94
5	20	PEG	1.4	120	80	69
6	15	PEG	1.4	120	80	52
7	25	DMSO	1.4	120	60	89
8	25	DMF	1.4	120	60	90
9	25	H_2O	1.4	Reflux	80	64
10	25	EtOH	1.4	Reflux	80	40
11	25	PEG	1.4	100	80	72
12	25	PEG	1.4	80	80	44

[a] Isolated yield.

In order to show the efficiency of Ni-SMTU@boehmite than corresponding homogeneous one, the homogeneous catalyst without boehmite nanoparticles (nPr-Si$(OMe)_3$-SMTU-Ni) and also S-methylisothiourea complex of Ni (SMTU-Ni) has been synthesized and their catalytic activity has been compared with Ni-SMTU@boehmite for the synthesis of 5-(2-chlorophenyl)-1H-tetrazole. The results of this comparison are shown in Table 2. As shown in Table 2, catalytic activity of heterogeneous and reusable catalyst (Ni-SMTU@boehmite) is comparable to their corresponding homogeneous ones, because: 1) the boehmite was formed in nanometer-sized particles (20-40 nm), which; when the size of the support is decreased to the nanometer scale, the surface area is substantially increased and the support can be evenly dispersed in the reaction mixture, forming a homogenous emulsion. 2) high-surface-area of boehmite nanoparticles including many hydroxyl groups leads to high catalyst loading capacity. Therefore, as shown in Table 2, these heterogeneous catalyst showed the advantages of both homogeneous (high catalytic activity) and heterogeneous (easy and rapid recoverability and recyclability) catalyst. Also, it is very important that the reaction did not proceed in the absence of catalyst even after long time (Table 2, entry 1).

Table 2. Comparison of Ni-SMTU@boehmite with corresponding homogeneous catalyst in the synthesis of 5-(2-chlorophenyl)-1H-tetrazole under optimized condition.

entry	Substrate	Catalyst	Time (min)	Yield (%)[a]
1	2-chlorobenzonitrile	-	80	Trace
2	2-chlorobenzonitrile	SMTU-Ni	55	91
3	2-chlorobenzonitrile	nPr-Si$(OMe)_3$-SMTU-Ni	60	92
4	2-chlorobenzonitrile	Ni-SMTU@boehmite	60	90

[a]Isolated yield.

After optimizing the reaction conditions, in order to explore the generality and scope of this protocol, various nitriles with NaN_3 were employed as substrates for the synthesis of 5-substituted 1*H*-tetrazole derivatives in the presence of Ni-SMTU@boehmite. The results of this study are summarized in Table 3. These results show that the reactions are equally facile with both electron-donating and electron-withdrawing substituents on the benzonitriles, resulting in good-to-high yields of the corresponding tetrazoles.

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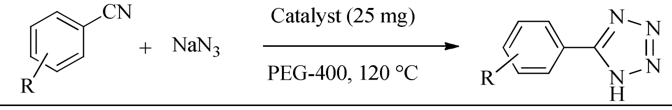
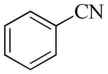
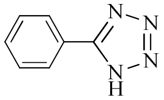
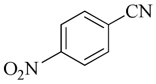
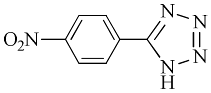
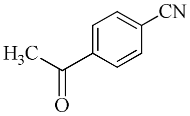
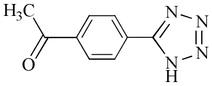
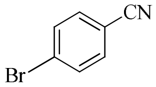
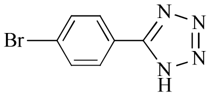
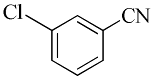
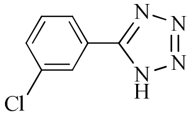
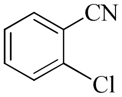
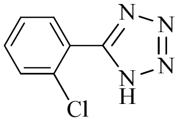
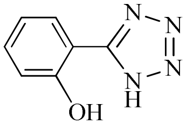
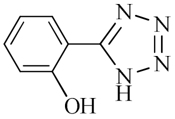
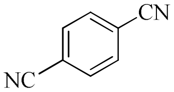
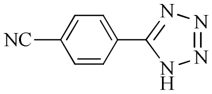
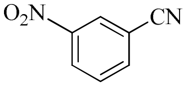
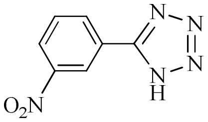
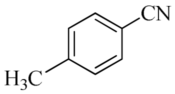
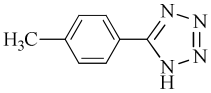
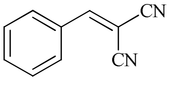
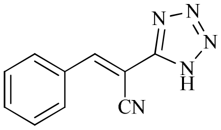
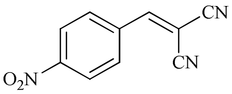
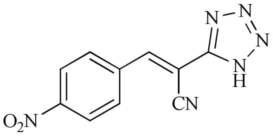
Table 3. Synthesis of 5-substituted 1*H*-tetrazole derivatives in the presence of Ni-SMTU@boehmite.



Entry	Nitrile	Product	Time (h)	Yield (%)[a]	Melting Point (ºC)
1			1.33	94	212-214
2			21	96	218-220
3			24	94	173-175
4			4	92	260-262
5			1.5	96	132-133
6			1	90	181-183
7			0.33	97	224-226
8			3.15	89	253
9			9	87	149-151
10			20	95	242-245
11			18	80	168-170
12			1	80	163-166

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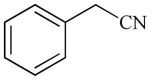
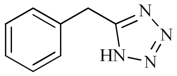
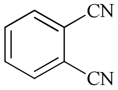
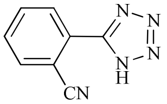
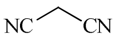
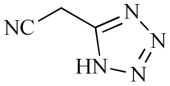
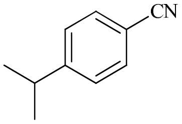
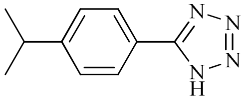
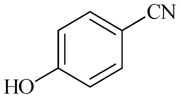
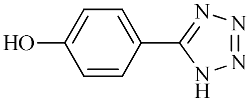
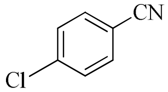
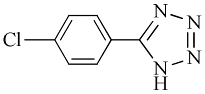
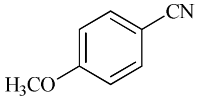
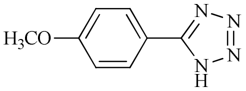
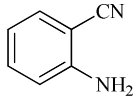
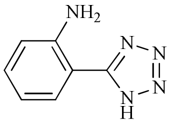
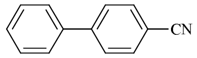
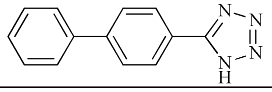
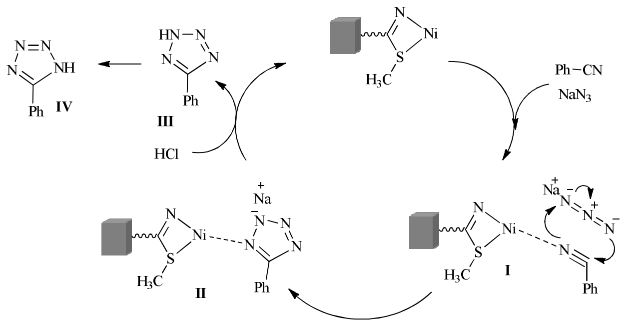
13			24	77	120-123
14			0.66	92	210-212
15			1.75	90	115-116
16			4.5	69	190-192
17			2.75	93	230-232
18			5	86	262-265
19			28	64	229-230
20			24	75	164-148
21			20	70	244-246

[a] Isolated yield.

A plausible mechanism for the synthesis of tetrazole derivatives catalyzed by Ni-SMTU@boehmite is shown in Scheme 3 [38, 39]. Initially, catalyst reacts with nitrile to produce the intermediate **I**; the [3+2] cycloaddition reaction between azide and **I** form the intermediate **II**; protonation of complex **II** HCl gives **III**, which rearranges to produce more stable desired product **IV**.



Scheme 3. Plausible mechanism for the synthesis of tetrazoles catalyzed by Ni-SMTU@boehmite.

In order to examine the efficiency of these procedures, we compared the results of the model reaction ([2+3] cycloaddition of benzonitrile with NaN$_3$) with the previously reported methods in the literatures (Table 4). This catalyst showed short reaction time and good yield than other reported catalysts in literatures. Also Ni-SMTU@boehmite is outstanding in terms of simple preparation, non-toxicity, price, stability and easy separation. As shown in Table 4, many previously reported catalysts have some drawbacks or limitations such as use of homogeneous catalysts that its separation is difficult from the reaction mixture, hazardous organic solvents and long reaction times. While, synthesis of tetrazoles in the presence of Ni-SMTU@boehmite has been carried out in PEG as green solvent with short reaction time. Also some of the previously reported catalysts are more expensive, requires high temperature or inert atmosphere, a lot of time and tedious conditions to prepare. While, boehmite nanoparticles was synthesized in water without inert atmosphere using commercially available materials. In addition, the number recycling of Ni-SMTU@boehmite is more than other catalysts. As shown in Figure 7, Ni-SMTU@boehmite was reused over 10 runs in synthesis of 2-(1*H*-tetrazol-5-yl)phenol without any significant loss of its catalytic activity or nickel leaching, which clearly demonstrates the practical reusability of this catalyst. Nickel leaching of Ni-SMTU@boehmite was studied by ICP-PEIS analysis and hot filtration test. Based on the obtained results from ICP-OES analysis, the amount of Ni in fresh catalyst and the recycled catalyst after 10 times recycling is 1.64 mmol g^{-1} and 1.31 mmol g^{-1}, respectively, which indicated that Ni leaching of this catalyst was very low. In order to examine leaching of nickel in reaction mixture and heterogeneity of this catalyst, we performed hot filtration in the reaction of 2-chlorobenzonitrile with NaN$_3$. In this study we found the yield of product in the half time of the reaction was 46%. Then the reaction was repeated and in half time of the reaction, the catalyst recovered and allowed the filtrate to react further. The

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yield of reaction in this stage was 50% that confirmed the leaching of nickel hasn't been occurred.

Table 4. Comparison results of Ni-SMTU@boehmite with other catalysts for synthesis of 5-phenyl-1*H*-tetrazole.

Entry	Catalyst	Condition	Time (h)	Yield (%)a	Ref.
1	CoY Zeolite	DMF, 120 ºC	14	90	[3]
2	Cu–Zn alloy nanopowder	DMF, 135 ºC	10	95	[4]
3	$B(C_6F_5)_3$	DMF, 120 ºC	8	94	[9]
4	CAN supported HY-zeolite	DMF, 110 ºC	4	93	[12]
5	$(NH_4)Ce(NO_3)_6$	DMF, 110 ºC	6	97	[13]
6	Fe_3O_4@SiO_2/Salen Cu(II)	DMF, 120 ºC	7	90	[16]
7	Fe_3O_4/ZnS HNSs	DMF, 120 ºC	24	81.1	[41]
8	Mesoporous ZnS	DMF, 120 ºC	36	86	[42]
9	$AgNO_3$	DMF, 120 ºC	5	83	[43]
10	$LiB(N_3)_4$	NH4OAc (15 mg), DMF/MeOH (9/1), 120 ºC	8	86	[44]
11	$Cu(OAc)_2$	DMF, 120 ºC	12	98	[45]
12	$CuFe_2O_4$	DMF, 120 ºC	12	82	[46]
13	$FeCl_3$–SiO_2	DMF, 120 ºC	12	79	[47]
14	Nano ZnO/Co_3O_4	DMF, 120-130 ºC	12	90	[48]
15	Ni-SMTU@boehmite	PEG, 120 ºC	1.33	94	This work

[a] Isolated yield.

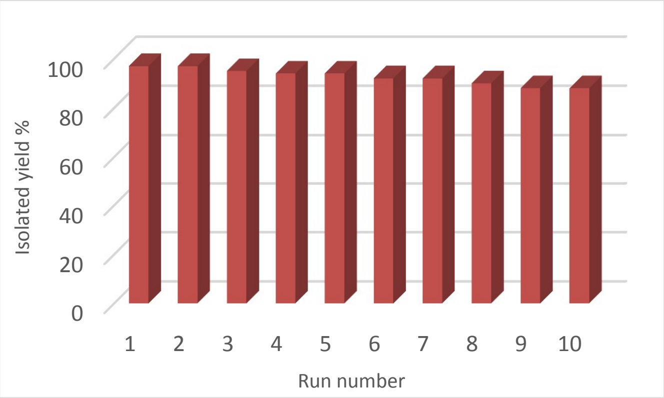

Figure 7. Recyclability of Ni-SMTU@boehmite in the synthesis of 2-(1H-tetrazol-5-yl)phenol.

3 Conclusions

In summary, Ni-SMTU@boehmite as a novel type of recoverable nanocatalyst was prepared by grafting of nickel on modified boehmite nanoparticles by very simple and inexpensive procedure without inert atmosphere. This catalyst was synthesized from inexpensive and commercially available starting materials. This catalyst has been characterized by FT-IR spectroscopy, TGA, XRD, ICP-OES, EDS, SEM and TEM techniques. The advantages of this protocol are the use of an eco-friendly, chemically stable and commercially available materials, the operational simplicity and good to high yields. More important, nanoboehmite is new support for heterogenization of homogeneous catalysts, which has several advantages such as high surface area, high stability, ease of surface modification, easy and inexpensive procedure of preparation. Also in this protocol, catalyst was reused for 10 times without Ni leaching or any significant loss of its catalytic activity. Heterogeneity of this catalyst has been studied using hot filtration and ICP-OES techniques. This catalyst showed excellent catalytic activity, high reusability and air or moisture stability for synthesis of 5-substituted 1*H*-tetrazole derivatives in PEG-400. Additionally, allylic, aliphatic and aromatic nitriles can also be used to synthesis tetrazoles using this catalyst. Thus, this methodology is effective for a wide range of nitriles for the synthesis of 5-substituted 1H-tetrazoles.

4 Experimental

4.1. Preparation of the Ni-SMTU@boehmite

The boehmite nanoparticles was synthesized according to our recently reported procedure *via* addition of aqueous NaOH solution to aqueous solution of $Al(NO_3)_3.9H_2O$ as drop to drop under vigorous stirring [36]. The obtained boehmite nanoparticles (1.5 g) was dispersed in 50 mL toluene by sonication for 30 min, and then 2.5 mL of (3-choloropropyl)triethoxysilane (CPTES) was added to mixture. The reaction mixture was stirred at 40 ºC for 24 h. Then, the prepared nanoparticles (nCl-Pr@boehmite) was filtered, washed with ethanol and dried at room temperature. The obtained nCl-Pr@boehmite (1g) were dispersed in 50 mL ethanol for 20 min, and then S-methylisothiourea hemisulfate salt (2.5 mmol) and potassium carbonate (2.5 mmol) were added to the reaction mixture and stirred for 28 h at 80 ºC. Then, the resulting nanoparticles (SMTU@boehmite) was filtered, washed with ethanol and dried at room temperature. The obtained SMTU@boehmite (0.5 g) was dispersed in 25 mL ethanol by sonication for 20 min, and then $Ni(NO_3)_2.6H_2O$ (1 mmol) was added to the reaction mixture. The reaction mixture was stirred at 80 ºC for 20 h. The final product (Ni-SMTU@boehmite) was filtered, washed by ethanol and dried at room temperature.

4.2 General procedure for the synthesis of 5-substituted 1H-tetrazoles

A mixture of sodium azide (1.4 mmol) and nitrile (1 mmol) in the presence of 0.025 g of Ni-SMTU@boehmite, was stirred at 120 °C in PEG-400; after completion of the reaction (observed by TLC), the reaction mixture was cooled down, and catalyst was isolated by simple filtration and HCl (4 N, 10 mL) was added to the filtrated solution. The products extracted with ethyl acetate (2×10 mL). The organic solvent was dried over anhydrous sodium sulfate, and concentrated to give the crude solid product.

4.3 Selected spectral data

5-Phenyl-1H-tetrazole (Table 2, Entry 1): White solid, m.p. 212-214 ºC, FTIR (KBr): vmax/cm^1: 3436, 2920, 1610, 1559, 1474, 1405, 1252, 1159, 1051, 987, 784, 689, 492. ^{1}H NMR (400 MHz, DMSO, ppm) δ = 7.65-7.59 (m, 3H), 8.08-8.04 (m, 2H).

5-(4-Nitrophenyl)-1H-tetrazole (Table 2, Entry 2): Yellow solid, m.p. 218-220 ºC, FTIR (KBr): vmax/cm^1: 3508, 3101, 2967, 2919, 2854, 2755, 2547, 1646, 1608, 1521, 1439, 1346, 1156, 1101, 1024, 951, 854, 721, 696, 494. ^{1}H NMR (400 MHz, DMSO, ppm) δ = 8.43-8.41 (d, J= 8.8 Hz, 2H), 8.31-8.29 (d, J= 8.8 Hz, 2H).

1-(4-(1H-tetrazol-5-yl)phenyl)ethanone (Table 2, entry 3): white solid, m.p. 173-175 ºC, FT.IR (KBr): vmax/cm^1 : 3432, 3144, 3079, 3011, 2969, 2921, 2858, 2719, 2625, 2472, 1680, 1570, 1431, 1365,

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1271, 1156, 1120, 1081, 1058, 997, 982, 961, 841, 752, 704, 589, 491. ^{1}H NMR (400 MHz, DMSO, ppm) δ =8.20-8.14 (m, 4H), 2.64 (s, 3H).

5-(4-Bromophenyl)-1H-tetrazole (Table 2, Entry 4): white solid, m.p. 260-262 ºC, FTIR (KBr): νmax/cm^{1}: 3443, 2956, 2923, 2861, 2766, 2627, 1601, 1423, 1317, 1152, 1055, 998, 842, 734, 562. ^{1}H NMR (400 MHz, DMSO, ppm) δ = 8.00-7.97 (m, 2H), 7.84-7.81 (m, 2H).

5-(3-Chlorophenyl)-1H-tetrazole) (Table 2, Entry 5): white solid, m.p. 132-133 ºC, FTIR (KBr): νmax/cm^{1}: 3454, 3241, 3063, 2972, 2894, 2605, 1972, 1651, 1473, 1445, 1360, 1300, 1246, 1094, 1002, 772, 675, 576. ^{1}H NMR (400 MHz, DMSO, ppm) δ = 8.09-8.00 (m, 1H), 8.04-8.01 (m, 1H), 7.69-7.63 (m, 2H).

2-(1H-tetrazol-5-yl)phenol (Table 2, Entry 7): white solid, m.p. 224-226 ºC, FTIR (KBr): νmax/cm^{1} : 3253, 3059, 2933, 2709, 2566, 2359, 1610, 1545, 1475, 1393, 1358, 1294, 1230, 1115, 1068, 946, 808, 742, 680, 541. ^{1}H NMR (400 MHz, DMSO, ppm) δ = 8.02-8.00 (m, 1H), 7.44-7.40 (m, 1H), 7.11-7.08 (m, 1H), 7.03-6.99 (m, 1H), 11.10 (br, 1H), 15.73 (br, 1H).

4-(1H-tetrazol-5-yl)benzonitrile (Table 2, entry 8): white solid, m.p. 253 ºC, FT.IR (KBr): νmax/cm^{1}: 3476, 3150, 3090, 3018, 2923, 2859, 2724, 2624, 2566, 2485, 2232, 1620, 1566, 1494, 1431, 1364, 1275, 1153, 1067, 1028, 847, 749, 695, 552. ^{1}H NMR (400MHz, DMSO, ppm) δ = 8.24-8.21 (m, 2H), 8.12-8.09 (m, 2H).

5-(3-Nitrophenyl)-1H-tetrazole (Table 2, Entry 9): White solid, m.p. 149-151 ºC, FTIR (KBr): νmax/cm^{1}: 3852, 3308, 3085, 2975, 2894, 2822, 2752, 1621, 1524, 1348, 1243, 1156, 1076, 1011, 912, 819, 727, 453. ^{1}H NMR (400 MHz, DMSO, ppm) δ = 8.85 (s, 1H), 8.50-8.43 (m, 2H), 7.94-7.90 (m, 1H).

Acknowledgements

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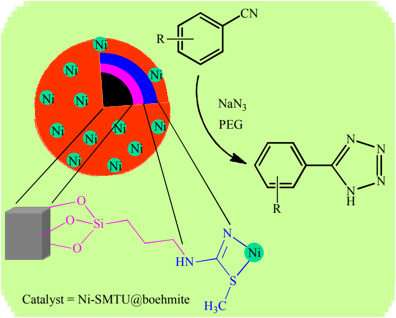
Graphical Abstract

Ni-S-methylisothiourea complex supported on boehmite nanoparticles and its application in the synthesis of 5-substituted tetrazoles

Arash Ghorbani-Choghamarani, Parisa Moradi and Bahman Tahmasbi



Boehmite nanoparticles were immobilized with a new type of nickel complex and applied for the synthesis of 5-substituted 1*H*-tetrazole derivatives in PEG-400.