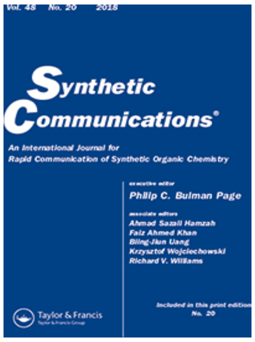

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Synthesis of tetrazoles, triazoles, and imidazolines catalyzed by magnetic silica spheres grafted acid

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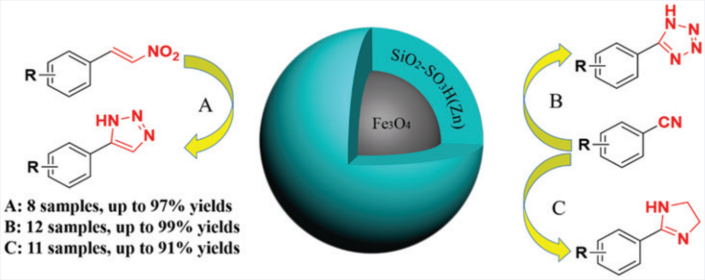
ABSTRACT

The magnetically separable catalysts are used in the synthesis of N-containing heterocycles, including tetrazoles, triazoles, and imidazolines. The magnetic silica sphere grafted sulfonic acid (MSS-SO_3H) is suitable for the synthesis of 1,2,3-triazole via the cycloaddition of nitroalkene with NaN_3, whereas the zinc-modified silica sphere catalyst (MSS-SO_3Zn) is more suitable for the synthesis of tetrazoles. The MSS-SO_3Zn catalyst also works well for the synthesis of 2-substituted imidazoline via the condensation of nitriles with ethylenediamine. Both of the MSS-SO_3H and MSS-SO_3Zn catalysts can be recovered easily by a magnet, and they can be reused without further tedious activation.

GRAPHICAL ABSTRACT



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KEYWORDS
Magnetically separable; silica sphere; imidazolines; triazoles; tetrazoles; heterocycles

Introduction

With the increasing development of catalytic synthesis strategies, the reusable catalysts have drawn much attention and resonated across numerous disciplines. In recent years, many magnetically separable catalysts have been developed for constructing versatile organic compounds via the C–C, C–X coupling reactions[1–4], and Fischer–Tropsch synthesis reactions.[5] Besides, the magnetic nanoparticles are also widely applied to remove phosphates from wastewater[6] and reduction of acetophenone.[7] The magnetically

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Supplemental data (full experimental detail and ^1H and ^{13}C NMR spectra) for this article can be accessed on the publisher's website.

separable nano-catalysts also hold an important position in the synthesis of heterocycles. For example, a graphene oxide/Fe_3O_4 supported Mo catalyst was reported to synthesize dihydropyridines efficiently, and this catalyst could be reused for eight times with no decrease in catalytic activity.[8] Similarly, the CeO_2-Fe_3O_4 nanoparticles catalyzed synthesis of benzoxazole and benzothiazole have also been presented.[9] Moreover, the Fe_3O_4 supported Cu was developed for the synthesis of quinazolinones and bicyclic pyrimidinones,[10] and a magnetic Pd-graphene catalyst was proved to be an efficient protocol for synthesizing 2-alkylquinolines.[11] The functionalized magnetic particles have been used in the synthesis of indole derivatives[12] and pyrazole-fused isocoumarins.[13] In this work, we applied two magnetically modified silica spheres catalysts to the synthesis of the triazoles, tetrazoles, and imidazolines. One is Fe_3O_4@SiO_2 grafted sulfonic acid catalyst (MSS-SO_3H), and the other is zinc-exchanged MSS-SO_3H named as MSS-SO_3Zn.

Results and discussion

The magnetic silica nanospheres were synthesized according to a typical method,[14, 15] then 3-mercaptopropyl trimethoxysilane (MPTMS) was employed to graft the –SH group on the silica sphere surface. The nanospheres were oxidized by H_2O_2, then the catalyst MSS-SO_3H was obtained. Stirring the MSS-SO_3H in a concentrated $Zn(NO_3)_2$ solution for 24 h at room temperature formed the zinc-exchanged catalyst MSS-SO_3Zn. The structure of two prepared materials was characterized by HR-TEM, EDS, and VSM analysis. From the Figure 1(a,b), we can find that the general size of the magnetic silica sphere is about 400 nm. Figure 1(c) indicates that the magnetic Fe_3O_4 is in the core position of the MSS-SO_3H, and it is coated with SiO_2. The edge of MSS-SO_3Zn is not as smooth as MSS-SO_3H because of doping of Zn. Figure 1(d–h) further demonstrates the structure of the nanoparticle was Fe_3O_4@SiO_2-SO_3Zn. Particularly, Figure 1(h) reveals that Zn mainly distributes on the catalyst's surface. Therefore, the structure presented in Figure 1(h) was confirmed as Fe_3O_4@SiO_2-SO_3Zn.

The magnetic property of the MSS-SO_3Zn and recycled MSS-SO_3Zn catalyst was investigated using a vibrating sample magnetometer at room temperature. As illustrated in Figure 2, the magnetization curves of the prepared materials exhibited tiny hysteresis loops, which demonstrated its paramagnetic characteristics. The magnetic intensity of recycled MSS-SO_3Zn is stronger than that of the fresh MSS-SO_3Zn, this may be due to the zinc leaching. Moreover, the catalyst can be separated by external magnetic field as illustrated in Figure S1.

First, the as-prepared catalyst MSS-SO_3H was applied to synthesize the triazoles, whose derivatives were used widely as the agricultural chemicals.[16] Typically, the synthesis of triazoles have been well developed by the Cu(I) catalyzed cycloaddition of organic azides with terminal alkynes.[17] To avoid the possible toxicity of residual cupric catalyst, nontoxic $BiCl_3$,[18] and metal-free protocol were also reported.[19] A more recent research reported an acid–base bifunctional heterogeneous catalyst.[20] In our study, a variety of triazoles have been synthesized through the condensation between nitroalkenes and sodium azide under the optimized reaction conditions (Table S1). As shown in Table 1, the magnetic silica sphere based catalyst MSS-SO_3H is highly effective

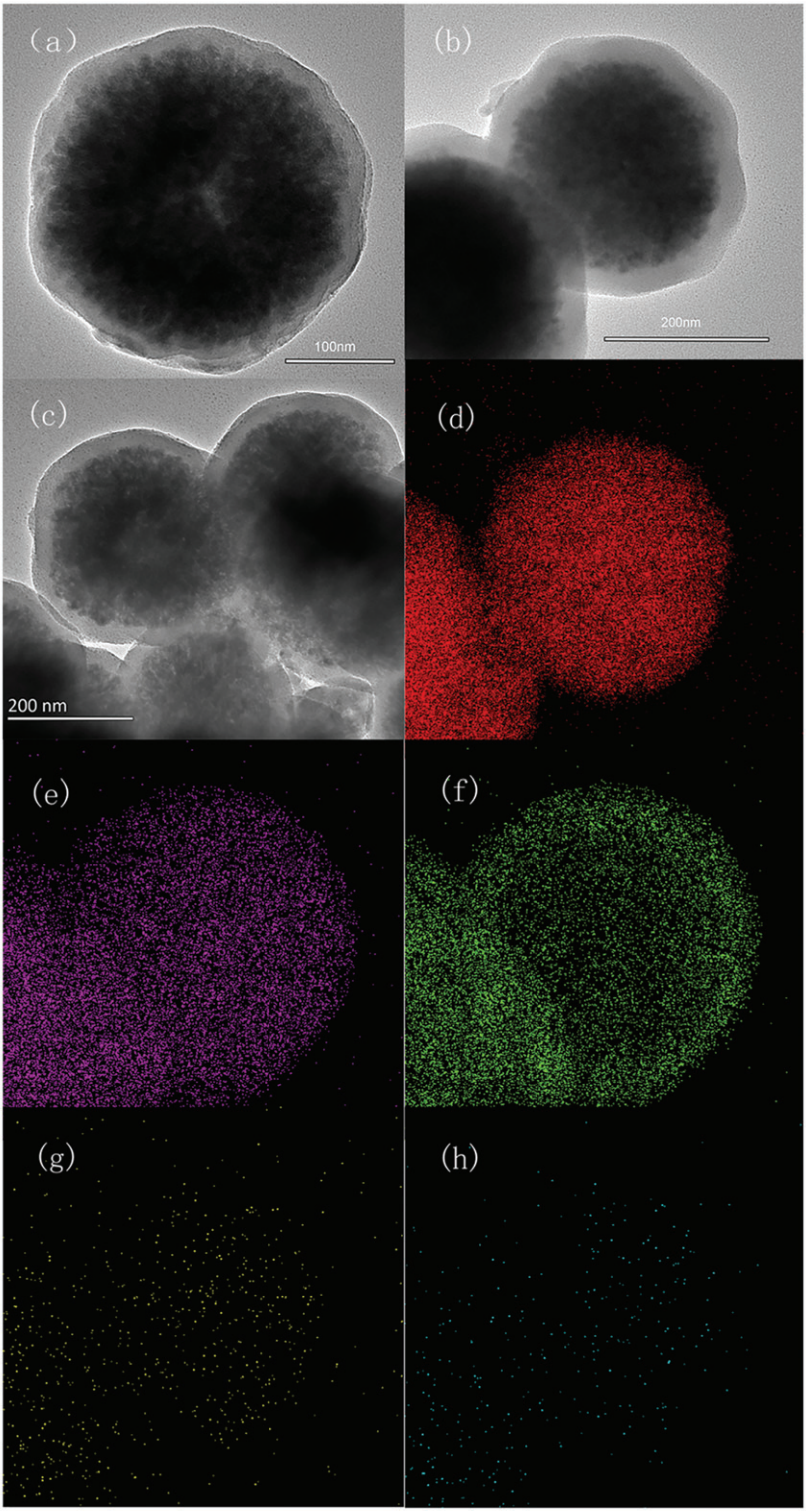


Figure 1. The morphology of MSS-SO3H and MSS-SO_3Zn: (a and b) HR-TEM of MSS-SO_3Zn (c) TEM of MSS-SO3H, EDS analysis of MSS-SO_3Zn: (d) Fe distribution (e) O distribution; (f) Si distribution (g) S distribution (h) Zn distribution.

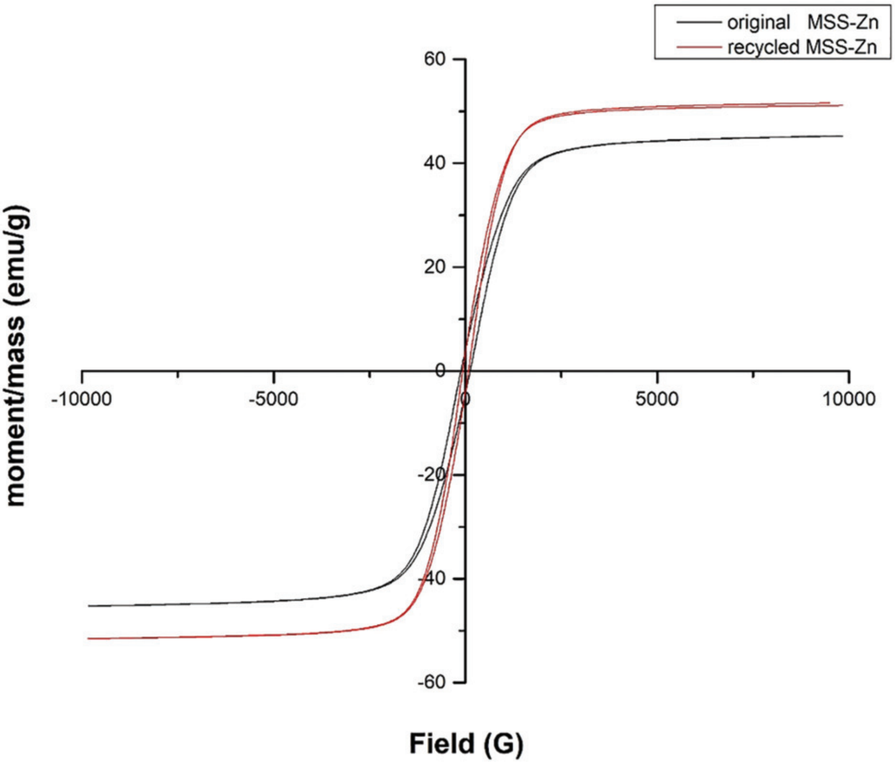


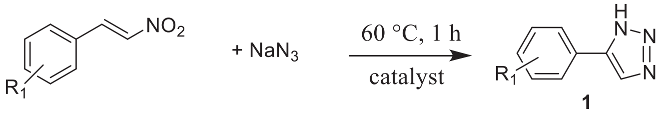
Figure 2. The VSM curses of MSS-SO_3Zn (a) and recovered MSS-SO_3Zn (b).

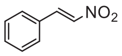
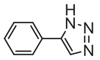
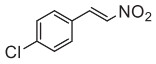
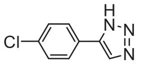
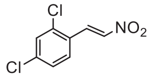
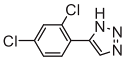
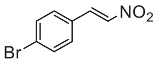
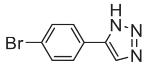
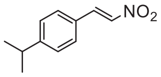
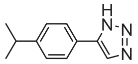
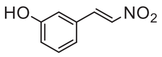
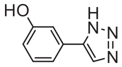
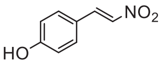
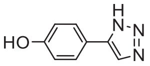
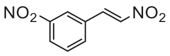
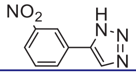
for most substrates to synthesize triazoles. The nitroalkenes bearing chloro, bromo, and isopropyl group gave excellent yields (**1a–1e**). The hindrance of ortho-substituted chloro atom led to a slightly declined yield (**1c**). The substrate bearing a strong electron-withdrawing $-NO_2$ gave 92% yield (**1h**), whereas the substrates bearing electron-donating group –OH (**1f**, **1g**) and isopropyl (**1e**) gave lower yields of 78%, 81%, and 83%. This suggested that the formation of 1,2,3-triazole might proceed a pathway of a $[3+2]$ cycloaddition, whereas the nitroalkene was the electrophiles.

With the successful application of MSS-SO_3H to the synthesis of triazole, we further investigated the cycloaddition of benzonitriles with sodium azide to synthesize tetrazoles, which were widely used in pharmacochemistry, coordination chemistry, photography, and agriculture fields.[21,22] The common method of preparing 5-substituted-1H-tetrazoles is the cycloaddition of nitriles with azide, and multitudinous catalysts have been reported such as Lewis acid $Cu_2(OTf)_2$,[23] $CdCl_2$,[24] $Fe(OAc)_2$,[25] $ZnCl_2$,[26] $AlCl_3$,[27] $FeCl_3$,[28] and heterogeneous catalysts such as nanoscale ZnS[29] and Cu_2O.[30] Even Br⊘nsted acids like HCl, NH_4Cl, and AcOH can be applied to synthesize tetrazoles via the cycloaddition of nitriles and azides.[31,32]

Considering the Br⊘nsted acidity of SO_3H and its potential to catalyze the cycloaddition of nitriles and azides, we applied MSS-SO_3H to synthesize 5-substituted-1H-teterazoles. To our delight, the MSS-SO_3H showed good efficiency for this reaction after optimizing the reaction conditions (Table S2). As listed in Table 2, some nitriles were

Table 1. Synthesis of triazoles catalyzed by MSS-SO_3H.[a]



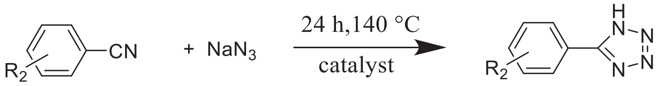
Entry	Substrate	Product	1	Yield/%
1			**1a**	97
2			**1b**	95
3			**1c**	80
4			**1d**	83
5			**1e**	83
6			**1f**	78
7			**1g**	81
8			**1h**	92

[a]Reaction conditions: 1 mmol α,β-unsaturated nitroarenes derivative and 2 mmol sodium azide, 60 °C, 1 h, 2 mL DMF as solvent, 10 wt% catalyst.

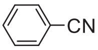
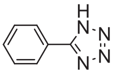
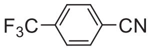
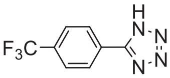
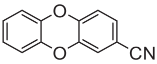
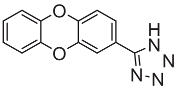
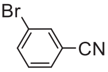
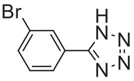
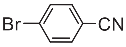
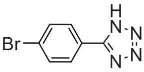
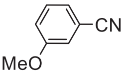
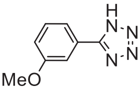
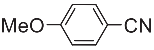
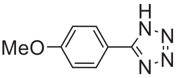
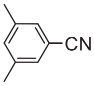
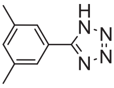
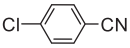
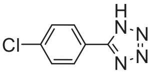
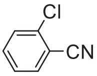
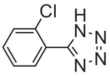
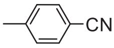
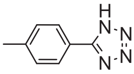
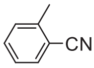
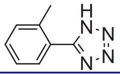
transformed into the target tetrazoles smoothly. Especially, the substrates bearing electron-withdrawing groups afforded corresponding target products in excellent yields, such as **2a–2d**. However, there were still some substrates could not offer satisfactory yields, such as **2e–2h**. In particular, more substrates bearing electron-donating groups afforded moderate to low yields. Considering the unsatisfactory yields of the target products, we modified the MSS-SO_3H catalyst by zinc-exchanging to promote the catalytic efficiency. As Table 2 shown, the zinc-exchanged MSS-SO_3H presented as MSS-SO_3Zn shows better performance in this reaction, it affords higher yields than MSS-SO_3H. Similarly, the yields of electron-deficient substrates (**2a–2e**) were much higher than that of electron-rich substrates (**2f**, **2g**). Meanwhile, we screened the substrates (**2i–2l**) and obtained the corresponding products in higher yields.

To explore more application of the MSS-SO_3Zn catalyst, we utilized MSS-SO_3Zn catalyst to synthesize the imidazolines, which were applied widely with synthetic intermediates, chiral auxiliaries, chiral catalysts, and ligands for asymmetric catalysis. The synthetic protocol is the cycloaddition of benzonitriles with ethylenediamine, which is a typical approach. The reactions were conducted under the optimistic conditions. (The

Table 2. Synthesis of tetrazoles using MSS-SO_3H(A) & MSS-SO_3Zn(B).[a]



2

Entry	Substrate	Product	2	Yield/%[b] with A	Yield/%[b] with B
1			**2a**	88	93
2			**2b**	94	99
3			**2c**	92	95
4			**2d**	99	98
5			**2e**	59	67
6			**2f**	36	55
7			**2g**	28	45
8			**2h**	52	67
9			**2i**	68	74
10			**2j**	47	56
11			**2k**	36	52
12			**2l**	28	56

[a] Reaction conditions, 2 mmol benzonitriles, 3.2 mmol sodium azide, 10 wt% of catalyst, 140 °C for 24 h.
[b] Isolated yields.

optimization is presented in Table S3). As Table 3 shown, the catalyst MSS-SO_3Zn offers moderate to good isolated yields of imidazolines in general. Both electron-donating and electron-withdrawing substrates could afford high conversions to target products, such as **3d** and **3i**. The phenylacetonitrile also gave the corresponding product in moderate yields (**3j**) and some other benzonitriles (**3f**, **3g**, and **3k**) also showed moderate to good conversions. The bromo atoms in **3b** and **3c** were substituted by –NH-CH_2CH_2-NH_2 because of the strong nucleophilicity of excess ethylenediamine.

Both of the MSS-SO_3H and MSS-SO_3Zn catalyst are magnetically recoverable. As Figure 3 shown, MSS-SO_3Zn catalyst exhibits higher catalytic activity than MSS-SO_3H for synthesizing tetrazoles but its reusability was lower than MSS-SO_3H due to the leaching of Zn. Anyway, a recovered MSS-SO_3Zn catalyst can regenerate its original catalytic activity by zinc ion exchanging. Moreover, MSS-SO_3H was suitable for synthesizing triazoles with high activity and reusability. However, the decreasing catalytic performance of MSS-SO_3H was also observed, that may due to the inevitable loss of catalyst nanoparticles during the work up. In a word, the catalytic activity of the two catalysts did not lose too much after six times runs. This means both of the catalyst MSS-SO_3H and MSS-SO_3Zn are stable enough for the synthesis of triazoles, tetrazoles, and imidazolines.

Experiments

Preparation of catalyst MSS-SO_3H and MSS-SO_3Zn

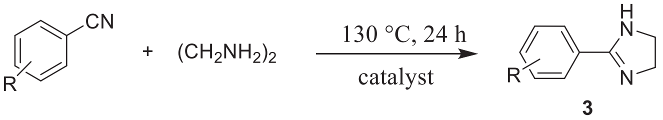
A portion of 0.2 g prepared Fe_3O_4 nanoparticles (method was introduced in the first part of Supplementary Materials) was treated by ultrasonic in the 0.1 M HCl solution for 10 min. Then, the activated Fe_3O_4 particles were dispersed into a mixture of 160 mL alcohol, 40 mL deionized H_2O, and 4 mL 25% $NH_3 \cdot H_2O$. After that, 1 mL tetraethoxylsilane (TEOS) was added into the above solution drop by drop, and the resulting mixture was stirred for 6 h. The magnetically collected solid was put into isopropanol (200 mL), then MPTMS (1 mL) was added into the liquid and the reaction was kept at 80 °C for 3 h to functionalize the silica surface with the thiol groups. The decanted functionalized silica sphere was put into 30 wt% H_2O_2 and stirred for 10 h under room temperature to form the sulfonic acid group. Finally, the catalyst MSS-SO_3H were obtained by clean-up and drying and its structure can be described by $Fe_3O_4@SiO_2$-SO_3H.

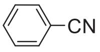
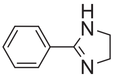
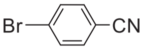
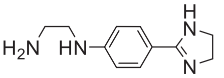
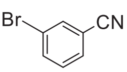
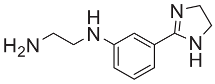
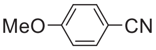
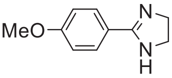
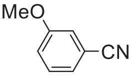
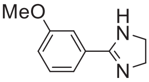
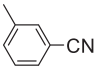
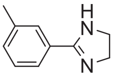
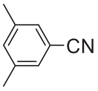
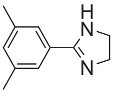
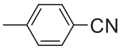
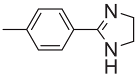
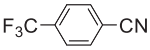
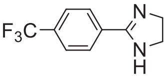
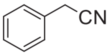
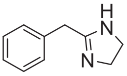
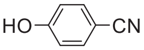
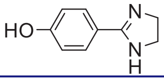
The fabrication of the catalyst MSS-SO_3Zn is described as below: the as-prepared catalyst MSS-SO_3H was stirred for 12 h in saturated $Zn(NO_3)_2$ alcohol solution. The obtained particles were cleaned with alcohol for three times and dried at 80 °C.

General procedure for the synthesis of triazoles (1a–1h)

A mixture of 10 wt% catalyst MSS-SO_3H, (2-Nitro-vinyl)-benzene derivatives (1 mmol), sodium azide (2 mmol) and DMF (2 mL) was added into a sealed tube, then heated for 1 h at 60 °C. After the catalyst was removed by magnetic separation (Figure S1), the solution was cooled and diluted with water, then extracted with ethyl acetate/petroleum ether for further evaporation. After evaporation, we obtained the isolated triazoles. A sample for characterization was purified on a flash silica column.

Table 3. Synthesis of imidazolines catalyzed by MSS-SO_3Zn.[a]



Entry	Substrate	Product	3	Yield/%
1			**3a**	83
2			**3b**	58
3			**3c**	67
4			**3d**	91
5			**3e**	25
6			**3f**	71
7			**3g**	69
8			**3h**	15
9			**3i**	85
10			**3j**	56
11			**3k**	56

[a] Reaction conditions: benzonitrile derivatives (1 mmol), ethylenediamine (2 mL), catalyst MSS-SO_3Zn (45 mg/mmol), 140 °C, 24 h, isolated yield.

5 -Phenyl-1H-1,2,3-triazole (1a)

White solid. M.P. 140–143 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (s, 1H), 7.85 (d, $J = 7.1$ Hz, 2H), 7.43 (d, $J = 7.8$ Hz, 2H), 7.32 (s,1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.3, 131.2, 129.0, 128.1, 127.4, 125.9. MS (ESI) m/z for $C_8H_7N_3$: 146 ($[M + H]^+$).

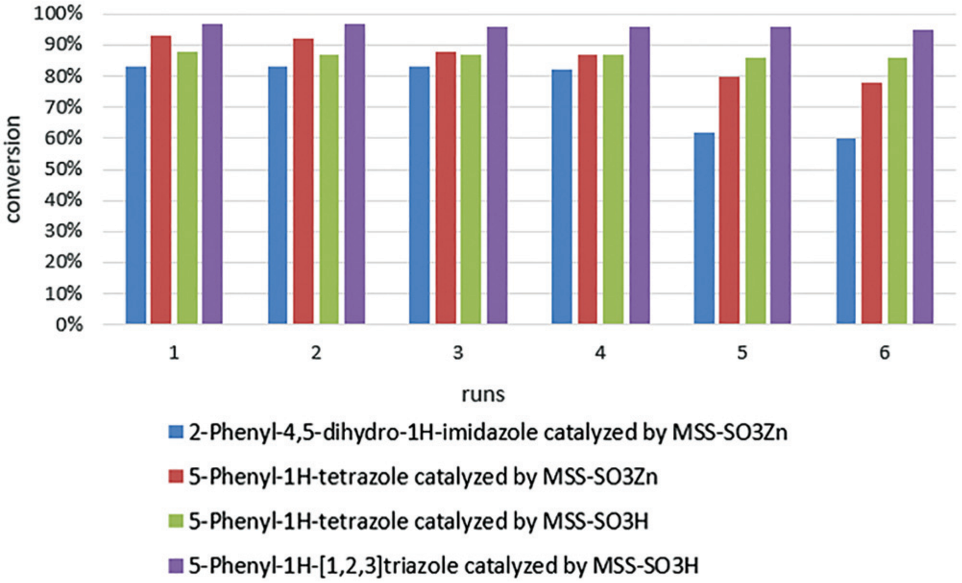


Figure 3. Recycling of the catalyst MSS-SO_3H and MSS-SO_3Zn for the synthesis of tetrazoles, tiazoles, and imidazolines.

General procedure for the synthesis of tetrazoles (2a–2l)

The benzonitrile derivatives (2 mmol), sodium azide (3.2 mmol), and DMF (2 mL) were mixed in a sealed tube, then 30 mg of catalyst MSS-SO_3H (or catalyst MSS-SO_3Zn) was added into the tube, which was heated for 24 h under 140 °C. After 24 hours' reaction, the catalyst was separated by magnetic force, and the solution was poured into water. The liquid was acidified to pH 1, then ethyl acetate was added to extract the tetrazoles. Carefully evaporating the solvent under reduced pressure, we got the isolated tetrazoles. A sample for characterization was purified on a flash silica column.

5 -Phenyl-1H-tetrazole (2a)

White solid; M.P: 216–217 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.64–7.65 (m, 3H), δ 8.07–8.10 (m, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.3, 130.3 129.9, 127.9, 126.8. HRMS: calcd. for $C_7H_8N_4$ $(M + H^+)$ 147.0665; found 147.0670.

General procedure for the synthesis of imidazolines (3a–3k)

The benzonitrile derivatives (1 mmol) and ethylenediamine (2 mL) were mixed in a sealed tube, then 45 mg of MSS-SO_3Zn catalyst was added. The mixture was heated at 130 °C for 24 h. After cooling, the catalyst was separated by magnetic force, and the organic layer was detached. Deionized water and dichloromethane were added into the organic liquid. The organic layer was evaporated to obtain the isolated imidazolines. A sample for characterization was purified on a flash silica column.

2 -phenyl-4,5-dihydro-1H-imidazole(3a)

White solid; M.P. 102∼103 °C; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.39–7.78 (m, 5H), 4.61 (s, 1H), 3.77 (s, 4H); ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 163.9, 130.9, 130.6, 128.5, 127.4, 49.9. MS (ESI) m/z for $C_9H_{10}N_2$: 147 ($[M+H]^+$).

Conclusions

In conclusion, we have developed two magnetically separable and reusable catalysts to synthesize imidazolines, tetrazoles, and triazoles. The grafted sulfuric acid based catalyst $Fe_3O_4@SiO_2\text{-}SO_3H$ (MSS-SO_3H) showed high activity in synthesizing triazoles, whereas the zinc-exchanged catalyst $Fe_3O_4@SiO_2\text{-}SO_3Zn$ (MSS-SO_3Zn) showed excellent performance in the synthesis of tetrazoles and imidazolines. Both of them can be recovered facilely by magnetic separation and reused for at least six runs. These heterogeneous catalysts were consistent with the concept of environmental friendliness.

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