

Recyclable Acid-Base Bifunctional Core-Shell-Shell Nanosphere Catalyzed Synthesis of 5-Aryl-NH-1,2,3-triazoles via "One-Pot" Cyclization of Aldehyde, Nitromethane and NaN₃

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Abstract: A magnetically separable core-shell-shell nanosphere $Fe_3O_4@nSiO_2-SO_3H@MS-NHCOCH_3$ has been fabricated as an acid-base collaborative catalyst for the three-component cyclization of aromatic aldehyde, nitroalkane, and sodium azide to afford NH-1,2,3-triazoles. The bifunctional heterogeneous catalyst takes advantages of high activity, good chemoselectivity and no toxic HN₃ releasing. A variety of aldehydes have been transformed to corresponding 5-aryl-NH-1,2,3-triazoles with up to 98% yield. Furthermore, the catalyst could be recycled by an external magnetic field and reused for many times without any activity lossing. Contrastly, a homogeneous catalyst system ammonium acetate/acetic acid also works to the three-component cyclization to afford NH-1,2,3-triazoles.

1,2,3-triazoles are a class of artificially synthesized fivemembered heterocyclic compounds, which have been widely applied in medicinal chemistry and material science.^[1] The synthesis of 1,2,3-triazoles has attracted extensive attention. So far, the most popular synthetic route is the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC).^[2] Besides of Cu, some other metal complexes also work, such as Ru and Ir, to give corresponding RuAAC and IrAAC reaction, respectively.^[3] To avoid the heavy metal residue in the products, non-toxic metal catalyst ^[4] and organocatalyst have been also developed.^[5]

In recent years, nitroolefin has been applied as an alternative of the terminal alkyne for the synthesis of 1,2,3-triazole.^[6] In many cases, the [3+2] cycloaddition of nitroolefin with NaN₃ gives the N-unsubstituted 1,2,3-triazoles, which have extensive applications in synthesizing various 1,2,3-triazoles by post-Nfunctionalization.^[7] However, the rare availability of nitroolefin drives the development of the "one pot" synthesis of 1,2,3triazoles with aldehydes, nitroalkanes and azides. What's more, the multicomponent reaction (MCR) is step-economical, and the separation of the intermediates is avoidable.^[8] In 2014, Dehaen's group detailed the synthesis of 1,2,3-triazole via the cascade reaction of organocatalyzed Henry condensation of the aldehyde with the nitro compound and the 1,3-dipolar cycloaddition of the azide to the in-situ generated nitroarene.^[9]

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reagent, aldehyde, and NaN3 was conducted.^[10] Recently, Lin and Chen individually developed the three-component reaction with aldehyde, nitroalkane and NaN3 in the presence of excess amounts of NaHSO₃/Na₂SO₃.^[11] or catalytic amount of aluminium(III) chloride.[12] These results not only make the synthesis of NH-1,2,3-triazoles easier, but also reveal that the three component condensation may be an acid-catalysed procedure. Nowadays, the heterogenization of homogeneous catalyst is in the trend of catalyst development, especially for the solid acid-base bifunctional catalysts that take advantage of both electrophile and nucleophile.^[13] Following this guideline, we developed the immobilized catalyst for the synthesis of 1,2,3triazoles via the MCR with aromatic aldehydes, nitroalkanes and NaN₃. Considering Sengupta reported in 2008 the prolinecatalyzed three-component reaction of *β*-alkyl nitroalkene to synthesize 1,2,3-NH-triazoles, [14] we recognize that an acidbase bifunctional catalyst will has good performance.

The designation of the target catalyst includes the following aspects: high efficiency, recoverability and easiness of catalyst preparation.^[15] Particularly, the chemoselectivity should be carefully considered. This is because that the selectivity of the condensation of aldehyde, nitroalkane with NaN₃ is not as good as the cycloaddition of alkyne with organic azides, which is well known as a "click reaction" and even heterogeneous catalyst such as Cu₂O and Au nanocrystals gives good chemoselectivity under mild conditions.^[16] Following these demands, we designed core-shell-shell structured heterogeneous catalvst Fe₃O₄@nSiO₂-SO₃H@MS-NHCOCH₃ (n stands for non-porous and MS stands for microporous SiO₂). It includes the combined highlights of the literatures.^[17] The core is the Fe₃O₄ sphere that give the catalyst magnetic separablity, the inner layer silica shell is grafted with -SO₃H that generates from the oxidation of -SH group, and the outer shell is functionalized with the acetylated -NH₂. The outer shell is punched to porous so that the reactant can reach the acid site. As expected, this core-shell-shell nanoparticles catalyse the synthesis of 1,2,3-triazole smoothly under mild conditions and the products are obtained with high vield..

The final bifunctional material $Fe_3O_4@nSiO_2-SO_3H@MS-NHCOCH_3$ was systematically characterized by TEM, EDS analysis, vibrating sample magnetometer (VSM), XRD, FTIR and N₂-adsorption-desorption.

As shown in the TEM images (Figure 1), the Fe₃O₄@nSiO₂-SO₃H@MS-NHCOCH₃ is uniform egg-like nanosphere with the average size of about 400 nm, and the three-layer structure is distinguishable. A selected particle (about 500 nm) is detailed with EDS analysis.

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Figure 1. (a and b) TEM images, (c, d, e and f) EDS elemental mappings of core-shell-shell structured catalyst

The distribution of Fe indicates that the Fe_3O_4 core is a solid ball, while the distribution of Si shows that the silica matrix is a hollow ball that is bigger than Fe_3O_4 core. The N sphere is a bit larger than the S sphere, this clearly presents that N locates in the outer silica shell and S is in the inner layer. The average thickness of silica shell is several tens of nanometres.



Figure 2. (a) Magnetization curves at 302 k of the catalyst. (b) Magnetic separation of the catalyst in ethanol.

The magnetic properties of the catalyst are shown in Figure 2. With an applied field of 10000 Oe, the saturation magnetization value is up to 50.004 emu/g (figure 2a). This indicates the high magnetization of the sample. The absence of hysteresis phenomenon demonstrates the superparamagnetic behavior of the material at room temperature. Figure 2b also shows that the well dispersed nanoparticles can be easily collected with an external magnetic field.



Figure 3. XRD and FTIR of Fe₃O₄@nSiO₂-SO₃H@MS-NHCOCH₃.

In order to further study the characteristics of Fe₃O₄@nSiO₂-SO₃H@MS-NHCOCH₃, the powder X-ray diffraction (XRD) was also conducted (Figure 3a). The diffraction peaks at 20= 18.6°, 30.2°, 35.8°, 37.4°, 42.3°, 53.8°, 57.1°, 62.9° and 74.3° correspond to the (111), (220), (311), (222), (400), (422), (511) (440) and (622) planes of cubic phase of Fe₃O₄ (JCPDS: 00-003-0862). And a wide diffusion peak at 20= 15-19° (marked with asterisk) generally was considered as the diffusion peak of amorphous silica. ^[18]

 Table 1. Optimization of the heterogeneous catalytic reaction conditions^[a].

PhCHO + CH ₃ NO ₂ + NaN ₃ \longrightarrow PhCHO + CH ₃ NO ₂ + NaN ₃					
1a	2a				' H 3a
Entry	Catalyst v (FS = Fe ₃ O ₄ @nSiO ₂)	Solvent	Temp. (°C)	Time (h)	Yield ^[b] (%)
1	FS-SO ₃ H@MS-NHAc	DMF	120	3	69
2	FS-SO ₃ H@MS-NHAc	CH ₃ OH	120	3	47
3	FS-SO ₃ H@MS-NHAc	CCl ₄	120	3	Trace
4	FS-SO ₃ H@MS-NHAc	DMF/CH ₃ OH	120	3	82 ^[c]
5	FS-SO ₃ H@MS-NHAc	DMF/CH ₃ OH	120	3	83 ^[d]
6	FS-SO ₃ H@MS-NHAc	DMF/CH ₃ OH	140	1	98
7	FS-SO ₃ H	DMF/CH ₃ OH	140	1	90
8	FS-NHAc	DMF/CH ₃ OH	140	1	50
9	FS-SO3H@nSiO2-NHAc	DMF/CH ₃ OH	140	1	62
10	-	DMF/CH ₃ OH	140	1	31

[a] Reaction conditions: benzaldehyde (106 mg, 1 mmol), nitromethane (122 mg, 2 mmol), NaN₃ (130 mg, 2 mmol) and catalyst (10 wt%), solvent (6 mL). [b] Yields of isolated products. [c] DMF (5 mL), CH₃OH (1 mL). [d] DMF (4 mL), CH₃OH (2 mL).

The surface chemical structure of the synthesized materials was characterized by FTIR spectroscopy (Figure 3b). The characteristic peak at 640 cm⁻¹ is due to the presence of Fe-O bond, and the peaks around 1087 and 509 cm⁻¹ are assigned to

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the characteristic SiO_2 bands. The presence of the sulfonyl group is confirmed in the spectrum because the peaks at 1309 cm⁻¹ was assigned to the stretching vibrations of the S=O. The peak at 1862 cm⁻¹ was assigned to imide asymmetrical carbonyl (C=O) absorbance. The bands around 2937 cm⁻¹ was assigned to the stretching vibrations of the CH₂ group. The broad peak centered around 3436 cm⁻¹ was an envelope of stretching vibrations for O-H of the silanol groups and the sulfonyl groups. These FT-IR spectra indicated that the sulfonyl groups and the amide groups were successfully grafted onto Fe₃O₄@nSiO₂.

We conducted the experiment of benzaldehyde, nitromethane and NaN₃ with the acid-base bifunctional catalyst in DMF, and the 1,2,3-triazole was obtained in excellent yield (table 1, entry 1). Because the catalyst contains amide that may acted the similar role towards DMF, we tried to replace the solvent with a low boiling point one so that the work-up could be easier. To our disappointment, the best solvent was still confined to DMF (entry 2-3). However, we found there was undissolved NaN₃ in DMF. and this might be a main reason that cause the incomplete conversion. When the solvent was pure methanol, sodium azide was completely dissolved but the problem was the serious impurities. We utilized the mixed solvent of DMF/methanol (5/1). which can fully dissolve sodium azide and maintain good conversion (entry 4-5). Raising the reaction temperature to 140 °C and shortening reaction time to 1 h led to a greatly increased yield (entry 6). The subsequent experiments revealed that the acidic group played a main role and acid-base synergy could obviously improve the catalytic effect. Under the same sphere conditions. the monofunctionalized magnetic $Fe_{3}O_{4}@nSiO_{2}\text{-}SO_{3}H$ offered relatively low yield of 90% 5phenyl-NH-1,2,3-triazole (entry 7). If the amide group was directly grafted on the Fe₃O₄@nSiO₂, the nanosphere was almost inactive without the existence of sulfonyl acid (entry 8). In the case of entry 9, its catalytic activity was equivalent to the one that contained only amide, because there was no pore in the outer imide grafted silica layer so that the reactants couldn't reach the acid sites. As the silicon matrix has amorphous hole by itself, the yield was actually a little higher than in entry 8. Obviously, a reaction in the absence of any catalyst gave a poor yield (entry 10). Treating the Fe₃O₄@nSiO₂-SO₃H@MS-NHAc in HCl to remove the protecting group -Ac gave no improvement, so we confirmed that the final catalyst should be the N-protected one, which provided better chemo compatibility than the Nunprotected catalyst.

To further evaluate the core-shell-shell nanosphere, we also explored the homogeneous AcOH/NH₄OAc catalysed the same reaction as a comparison. The optimization of the homogeneous conditions was concluded in the table S1.

Under the optimized reaction conditions, various aldehydes were subjected to this one-pot reaction with nitromethane and sodium azide. The results are summarized in table 2. All substrates afforded the target product in excellent yields. The effect of electron-withdrawing or electron-donating group on the reaction was not apparent.

For most aldehydes, the corresponding NH-1,2,3-triazoles were obtained with more than 90% yield according to the general procedure (3a, 3b, 3c, 3g, 3h, 3i, conditions A), and the others gave more than 80% product (3d, 3f, 3j-3n), except the cyano benzaldehyde that gave 3e. This is because 1 mmol NaN₃

was used to inhibit the formation of corresponding tetrazole, as both of the aldehyde group and the cyano group can react with sodium azide in the presence of acid to generate triazole and tetrazole respectively. Considering the formation of triazole is faster than tetrazole, a small amount of NaN3 was used. Especially, acquiring the product 3n was very exciting, because it couldn't be obtained by using HOAc/NH₄OAc as catalyst. No matter whatever the reaction conditions changed, the TLC always showed us that a large amount of impurities existed in the reaction solution and no main product. Generally, the HOAc/NH₄OAC catalyzed three-component reaction (conditions B) was also an acceptable method for the synthesis of 5-aryl-NH-1,2,3-triazoles via the multicomponent reaction of aldehyde, nitromethane and NaN₃, because the catalyst is easilv accessible and the functional group tolerance is wide.

 Table 2. Substrate scope of the catalytic reaction to afford NH-1,2,3-triazoles.



Reaction mixtures: aromatic aldehydes (1 mmol), nitroalkanes (2 mmol), NaN₃ (2 mmol) and CH₃OH (1 mL), DMF(5 mL). The reactions were heated at 140 °C with bifunctional catalyst (10 wt%) for 60 min (conditions A) or 8equiv. HOAc and 1 equiv. NH₄OAc for 80min (conditions B). Yields of isolated products are given. ^a: The dosage of NaN₃ was 1 mmol.

Comparing with the HOAc/NH₄OAc systems, the heterogeneous catalyst $Fe_3O_4@nSiO_2-SO_3H@MS-NHCOCH_3$ showed many advantages such as high yield, excellent selectivity and safety. In most cases, the bifunctional solid catalyst gave higher yield than the HOAc/NH₄OAc. We could obtain excellent yields when we adopt 10 wt% catalyst that is only 10-20 mg/mmol, and the amount of catalyst is insensitive. That embodied remarkable performance of the catalyst. Again, the acid center is grafted on the inner silica sphere, this prevent the release of hydrazoic acid, which generates in situ and is a

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highly toxic substance that can inhibit enzyme activity and cause nerve change. That reflects the safety of heterogeneous catalyst.



Figure 4. (a) The crystallization of 5-(4-isopropylphenyl)-1H-1,2,3-triazole. (b) The recyclability of the catalyst.

Another advantage of our heterogeneous catalyst is that less impurities generates than homogeneous catalytic system, which can be proved in the work-up process. As quite a few byproducts could format during the cyclization of nitroolefin with sodium azide, the previous reports have alleged that NH-1,2,3triazoles can't be crystallized out.[6a] Good chemoselectivity that was observed on TLC and HPLC interested us to challenge the crystalizing ability of the reaction mixture, as it is well accepted that less impurities offer better crystal ability. We chose the reaction of p-isopropylbenzaldehyde as the objective reaction. On completion of the reaction, the catalyst was separated out and the solution was mixed with double volume of water then was refrigerated overnight. The product was crystallized out in the end as we can see in Figure 4a. This may because the bulky byproducts is limited by the microtunnel of the catalyst, which matched with the N₂-adsorption-desorption experimental results (Figure 5). The curve indicates the low N₂ adsorption of the catalyst, and this reveals that there was almost no mesopores or macropores in the nanoparticles. Considering the result of cyclization using a non-porous catalyst (table 1, entry 9), there must be pores in the outer silica shell, therefore the pores should be in microscale. This may be mutually deduced from the low CTAB loading in the preparation of the outer shell.

The main advantage of the heterogeneous catalyst is that can be reused many times without any loss of the catalytic activity. The recyclability of our catalyst was investigated in the synthesis of 5-phenyl-NH-1,2,3-triazole at the optimized reaction conditions. The catalyst can be retrieved via magnetic separation, lavation with ethanol and drying, then used for next reaction cycle. The recycling test showed that the catalyst was robust and could be reused up to 10 times without any loss in catalytic activity (Figure 4b).

As we concluded, the good reusability located in two aspects: one is that the active centers of the catalyst are organic functional groups that are linked to the silica matrix through the strong covalent bond, so no active component leaches out during the reactions. The other one is that our catalyst is robust enough and can be retrieved by a magnet bar at the end of reaction, so it can be thoroughly recovered without any losing. The TEM image of the recovered catalyst in Figure S1 confirmed that the morphology of the sample was almost unchanged.



Figure 5. Nitrogen adsorption-desorption curve.

Because we found the intermediate nitroolefins present both in homogeneous and heterogeneous catalytic system, we speculated that the reaction path is a one-pot two-steps pathway that includes a Henry condensation and a 1,3-dipolar cycloaddition cascade reaction as described in the earlier literature.^[19] The heterogeneous reaction was expected to proceed through the following pathway (Scheme 1). The acid site activates the benzaldehyde through the hydrogen bond between the carbonyl group and the proton of sulfonyl acid, while the amide-activated nitromethane attacks the activated benzaldehyde to form the β -nitro-alcohol, which converts to nitroolefin by eliminating one molecular water under heating. The second step is that the triazoline is formed via the cycloaddition of the olefin and azide. The elimination of HNO₂ gives the triazole as the ultimate product. The bifunctional catalyst was involved in all of the reaction process and participated in the next run with its original form. In order to verify the reaction process, we carried out DSC testing with the HOAc/NH₄OAc catalyzed model reaction (Figure S2). The curve shows two exothermic peaks, this indirectly verified the mechanism of two steps.



Scheme 1. Proposed reaction pathway for the synthesis of 5-aryl-NH-1,2,3-triazoles in heterogeneous catalytic system.

In conclusion, we have developed an efficient heterogeneous Fe₃O₄@nSiO₂-SO₃H@MS-NHCOCH₃ catalyst for the multicomponent condensation of aldehyde, nitroalkane and sodium azide. This process gives 5-aryl-NH-1,2,3-triazoles with excellent yields and has showed a wide substrate scope. A homogeneous catalytic system HOAc/NH₄OAc also works, but the heterogeneous catalyst provides better yield because the micro tunnel of the silica shell limits the generation of byproducts. Moreover, the application of the silica matrix wrapped acid enhances the operating security. In addition, its good magnetism and structure stability can guarantee catalytic activity does not decline even after it is used repeatedly for many times.

Experimental Section

Preparation of Fe₃O₄@nSiO₂-SH.First, Fe₃O₄ (0.2 g) was treated by 0.1 mol/L HCl solution (60 mL) under ultrasonic condition for 10 minutes. The activated magnetic nanoparticles were dispersed in the homogeneous solution of deionized H₂O (40 ml), ethanol (160 mL), and 25% NH₃·H₂O (4 mL). After TEOS (1 mL) was added dropwise, the solution was stirred vigorously at ambient temperature for 6 h. Then, the solid was separated from the suspension then reacted with MPTMS (1 mL) in isopropanol (200 mL) at 80 °C for 3 h to functionalize the silica surface with thiol groups. Finally, the Fe₃O₄@nSiO₂-SH nanocomposite was segregated by an external magnet and washed with ethanol for a few times

Preparation of Fe₃O₄@nSiO₂-SH@nSiO₂-NHCOCH₃. Along with the addition of TEOS (1.5 mL), the Fe₃O₄@nSiO₂-SH was stirred in a mixture of ethanol (160 mL), deionized water (40 mL) and CTAB (0.3 g) at room temperature for 6 h. After the liquid was removed, the residue was blended with isopropanol (200 mL) and APTES (1.5 mL) at 80 °C for 3 h. As the solution was cooled to room temperature, the solid was attracted by a magnet to remove the liquid and washed with little CCl₄. Eventually, the Fe₃O₄@nSiO₂-SH@nSiO₂-NHCOCH₃ was prepared by reacting the above obtained magnetic materials with acetic anhydride (4 mL) in CCl₄ at 80 °C for 4h.

Typical Procedure for the synthesis of NH-1,2,3-triazoles. The mixture of aromatic aldehydes (1 mmol), nitromethane (2 mmol), NaN₃ (2 mmol), DMF (6 ml) and acid-base bifunctional catalyst (10 wt %) was stirred in a sealed tube at 140 °C. After 60-80 min (as monitored by TLC), the solution was quenched with H₂O (20 mL) and extracted with EtOAc (4×10 mL). The combined organic layers were dried through adding anhydrous Na₂SO₄, and the solvent was evaporated in vacuo. The resulting mixture was purified by flash column chromatography on silica gel (SiO₂, petroleum ether/EtOAC) to afford the NH-1,2,3-triazoles.

In a compared procedure, the mixture of acetic acid (8 mmol) and ammonium (1mmol) was used as the alternative of the heterogeneous catalyst following the similar procedure. This system also worked well in the synthesis of NH-1,2,3-triazoles.

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Recyclable Acid-Base Bifunctional Core-Shell-Shell Nanosphere Catalyzed Synthesis of 5-Aryl-NH-1,2,3-triazoles via "One-Pot" Cyclization of Aldehyde, Nitromethane and NaN₃

- Fe $_3O_4@nSiO_2-SO_3H@MS-NHCOCH_3$ as an recyclable heterogeneous catalyst
- The reaction is safe to be handled as no dangerous hydrazoic acid releases.
- The NH-1,2,3-triazoles are synthesized from aromatic aldehydes, nitromethane and sodium azide with less byproducts.
- The catalyst can be reused for ten times without any loss of the catalytic activity.