



Efficient synthesis of α -aminonitriles over homopiperazine sulfamic acid functionalized mesoporous silica nanoparticles (MSNs-HPZ-SO₃H), as a reusable acid catalyst

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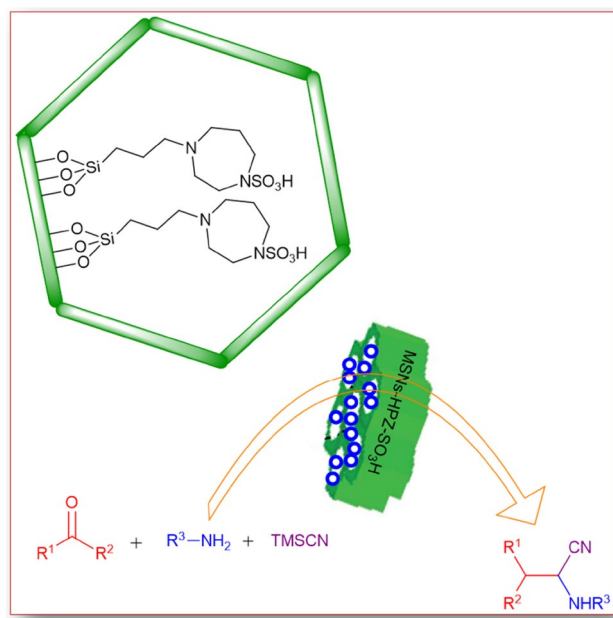
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Abstract

Good to excellent yields of α -aminonitriles are achieved through three-component Strecker reaction of aldehydes or ketones with amines and trimethylsilyl cyanides over homopiperazine sulfamic acid functionalized mesoporous silica nanoparticles (MSNs-HPZ-SO₃H). The advantages of this protocol include: simplicity, short reaction time, high yields, ease of product isolation and reusability of the catalyst.

Graphical abstract

MSNs-HPZ-SO₃H is prepared as an acid catalyst and successfully used for three-component Strecker reaction of aldehydes or ketones with amines and trimethylsilyl cyanides (TMSCN) under solvent-free conditions, a straightforward strategy for the synthesis of α -aminonitriles.



Mohamad Z. Kassaee: Visiting Scholar (sabbatical).

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Keywords α -Aminonitriles · Homopiperazine · Mesoporous silica · Nanocatalyst · One-pot synthesis

Introduction

A fundamental aspect of the green chemistry is adoption of multi-component reactions (MCRs) with atom efficiency and significant diversity plus straightforward design, and formation of multi-bonds in one pot [1]. An important multi-component reaction is the one-pot three-component synthesis of α -aminonitriles, which are valuable synthons in synthesis of various nitrogen-containing heterocycles such as imidazoles, thiadiazoles [2], 4-amino-2,3-dihydroisothiazole-1,1-dioxides [3] and aza spiro nucleoside analogous of TSAO [4]. They are also regarded as possible precursors to corrins, porphyrins, nucleic and nicotinic acids [5] and saframycin A [6]. In fact, α -aminonitriles have been considered as key intermediates for the synthesis of natural, unnatural α -amino acids [7] and the chiral building blocks in the pharmaceutical industry [8]. The Strecker reaction is one of the known methods for preparation of α -aminonitriles [9]. This classical procedure involves a direct multi-component reaction using an aldehyde or ketone, an amine or its equivalent and a cyanide reagent. Among cyanide sources for the synthesis of α -aminonitriles, trimethylsilyl cyanide (TMSCN) [10] is a safer reagent. Due to the importance of the Strecker reaction products (α -aminonitriles), numerous modifications and improvements have been done to perform this reaction with various protocols which often require a Bronsted or Lewis acid catalytic system. Thus, various homogeneous catalysts have been developed in recent years including: vanadyl triflate [11], Sc(OTf)₃ [12], NiCl₂ [13], InI₃ [14], RhI₃ [15] and GdCl₃·6H₂O [16]. On the other hand, to overcome the problems associated with homogeneous catalysts, several heterogeneous catalysts have been reported including: silica-based scandium(III) [17], SO₄²⁻/ZrO₂ [18], [bmim]BF₄ [19], sulfamic acid functionalized magnetic Fe₃O₄ nanoparticles [20], MNPs functionalized with urea or urethane moieties [21], SBA-15-supported sulfonic acid [22], NHC–amidate Pd(II) complex [23], mesoporous aluminosilicate [24], guanidine hydrochloride [25], K₂PdCl₄ [26], chitosan [27], β -cyclodextrine [28], Sn–montmorillonite [29], Co/SBA-15 [30], PEG-OSO₃H

[31], [VO(TPPA)][C(CN)₃]₄ [32] and montmorillonite KSF clay [33].

During the last few years, acid catalysts have played an important role in organic transformations. Despite the high activity and selectivity, the use of homogeneous acidic catalysts has been somewhat limited because of drawbacks which have led to economical and environmental problems. Therefore, heterogeneous acidic catalysts may overcome these problems. The immobilization of homogeneous catalysts on a solid support has advantages such as simple separation, minimization of waste and less contamination.

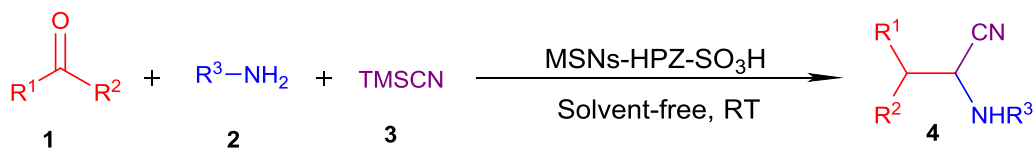
Mesoporous material properties include high surface area, tunable pore size distribution, high hydrothermal and mechanical stability which make them a potential candidate as a catalyst support in the field of heterogeneous catalysis [34–36]. Recently, we have prepared MSNs-HPZ-SO₃H and used it as a catalyst for synthesis of 1-amidoalkyl-2-naphthols [37]. Herein, we wish to report an efficient procedure for synthesis of α -aminonitriles via one-pot three-component condensation of aldehydes or ketones, amines and TMSCN in the presence of MSNs-HPZ-SO₃H as an efficient solid acid catalyst (Scheme 1).

Results and discussion

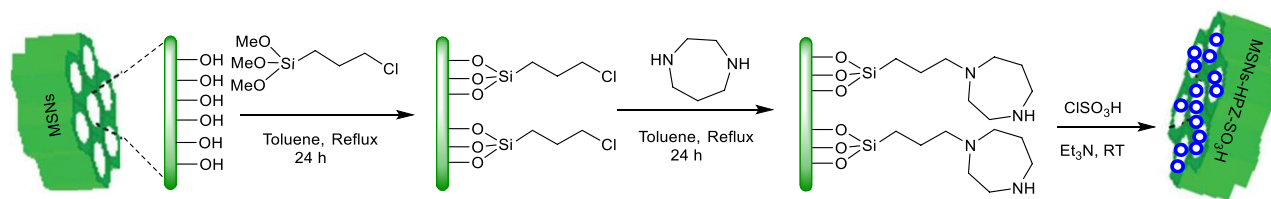
The MSNs-HPZ-SO₃H is prepared using the following procedure (Scheme 2) [37]. In the first step, mesoporous silica nanoparticles (MSNs) are prepared via the sol–gel method [38]. In the second step, 3-chloropropyl-functionalized (MSNs-Cl) is obtained from reaction of MSNs with 3-chloropropyltrimethoxysilane (CPTMS). Reaction of MSNs-Cl with homopiperazine gives MSNs-HPZ. Finally, reaction of the latter with chlorosulfonic acid (ClSO₃H) gives the nanocatalyst (MSNs-HPZ-SO₃H).

The synthesized catalyst is characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric/differential thermal analyses (TGA-DTA) and nitrogen adsorption–desorption analysis.

The XRD pattern of pure MSNs is assigned to (100), (110) and (200) planes with values of *d*-spacing at 40.01,



Scheme 1 Solvent-free Strecker reaction of carbonyl compounds (1), amines (2) and TMSCN (3) over MSNs-HPZ-SO₃H, at room temperature



Scheme 2 Preparation of the nanocatalyst (MSNs-HPZ-SO₃H)

26.97 and 22.46 Å, respectively. For MSNs-HPZ and MSNs-HPZ-SO₃H, only a reflection associated with (100) plan of the ordered 2D hexagonal mesophase is observed. The intensity of this reflection after functionalizing with organic groups is lower than that of the original MSNs (Fig S1, Supporting Information).

The FT-IR spectra of MSNs, MSNs-Cl, MSNs-HPZ and MSNs-HPZ-SO₃H are compared (Fig S2, Supporting Information). In the spectrum of starting MSNs, characteristic absorption bands at 1086 cm⁻¹ and 801 cm⁻¹ are assigned to asymmetric and symmetric stretching vibrations of Si–O–Si. Also, stretching of Si–OH at 962 cm⁻¹ and bending of Si–O–Si at 461 cm⁻¹ are observed. The broadband of 3450 cm⁻¹ is related to the stretching vibrations of silanol groups, and the peak at 1635 cm⁻¹ is assigned to the H–O–H bending vibration of the absorbed water molecules on surface. Stretching vibrations of anchored alkyl groups appear as weak C–H symmetric and asymmetric absorptions at 2930 and 2960 cm⁻¹, respectively. In addition, N–SO₂, O–SO₂ and S=O bonds stretching vibrations cannot be resolved due to the overlap with the Si–O–Si stretching at 960–1350 cm⁻¹. Broad peak in the range of 2500–3600 cm⁻¹ indicates the acidic OH vibration signal of SO₃H group. Also, a new band at approximately 580 cm⁻¹ is due to the presence of a SO₂ group in MSNs-HPZ-SO₃H.

SEM image provides more accurate information about the morphology and particle size of the MSNs-HPZ-SO₃H nanocatalyst (Fig S3, Supporting Information). This micrograph indicates that the particle morphology is relatively semi-spherical. Also, the obtained histogram of the SEM image confirms that the size distribution is narrow with a 23 nm average value and a 17 nm standard deviation.

Thermogravimetric/differential thermal analyses (TGA/DTA) of MSNs-HPZ-SO₃H display the thermal stability of the synthesized material (Fig S4, Supporting Information). The initial weight loss from 25 to 120 °C is due to the removal of physically adsorbed water and solvent on the external surface of the nanoparticles. The weight loss between temperature ranges of 200–670 °C in the TGA curve may be associated with oxidative decomposition of organic and inorganic functional groups. On the basis of

these results, the well grafting of organic functional groups on the MSNs is verified.

The textural properties of MSNs and MSNs-HPZ are probed (Fig S5, Supporting Information). The isotherms of these two materials exhibit type IV curve, showing the characteristic of uniform mesoporous materials. The calculated Brunauer–Emmett–Teller (BET) surface area, pore volume and pore diameter of MSNs are 783 m²/g, 0.767 cm³/g and 3.9 nm, respectively. After being grafted, the corresponding parameters for MSNs-HPZ are decreased to 313 m²/g, 0.175 cm³/g and 2.2 nm, respectively. These observations suggest that the organic groups are successfully anchored on the primary mesopores.

Catalytic ability of MSNs-HPZ-SO₃H is tested for the exclusive synthesis of α-aminonitrile derivatives. To explore the optimized conditions, the reaction of benzaldehyde with aniline and TMSCN is chosen as a model reaction, and the effects of various solvents and catalyst amounts are investigated. The initial screening of the reaction in the presence of different amounts of catalyst in various times shows that the best result is obtained in the presence of 10 mg catalyst when reaction reaches 92% yield in 10 min under solvent-free conditions. In the absence of the catalyst, reactivity is poor and provides low yield for the model reaction (Table 1). To compare the effects of solvents with that of solvent-free conditions, we evaluate the reaction in the absence and presence of solvents such as EtOH, CH₃CN, CH₂Cl₂ and H₂O.

Table 1 Effect of the catalyst amount in the reaction of benzaldehyde, aniline and TMSCN at room temperature

Entry	Catalyst (mg)	Time (min)	Yield (%) ^a
1	0	300	Trace
2	5	20	60
3	5	30	75
4	10	10	92
5	15	10	92
6	20	10	93

Bold row indicate the best result obtain by using 10 mg catalyst

^aIsolated yields

Table 2 Solvent effects and temperature on reaction of benzaldehyde, aniline and TMSCN

Entry	Solvent ^a	Temperature (°C)	Time (min)	Yield (%) ^b
1	EtOH	RT	120	65
2	CH ₃ CN	RT	120	50
3	CH ₂ Cl ₂	RT	120	45
4	H ₂ O	RT	120	70
5	Solvent-free	RT	10	92
6	Solvent-free	50	10	91
7	Solvent-free	80	10	93

Bold row indicate the best result obtain under solvent-free conditions

^a2 ml solvent is used

^bIsolated yields

Solvent-free conditions are found more suitable, on the basis of reaction time and yield at room temperature (Table 2).

Optimal reaction conditions are established to show the scope and generality of this process. So, three-component condensation of other substituted aldehydes and amines, with TMSCN over MSNs-HPZ-SO₃H, is carried out under the same reaction conditions. The results show a highly effective performance of the catalyst in the preparation of α -aminonitriles (Table 3). Various benzaldehydes with substituents carrying either electron-donating or

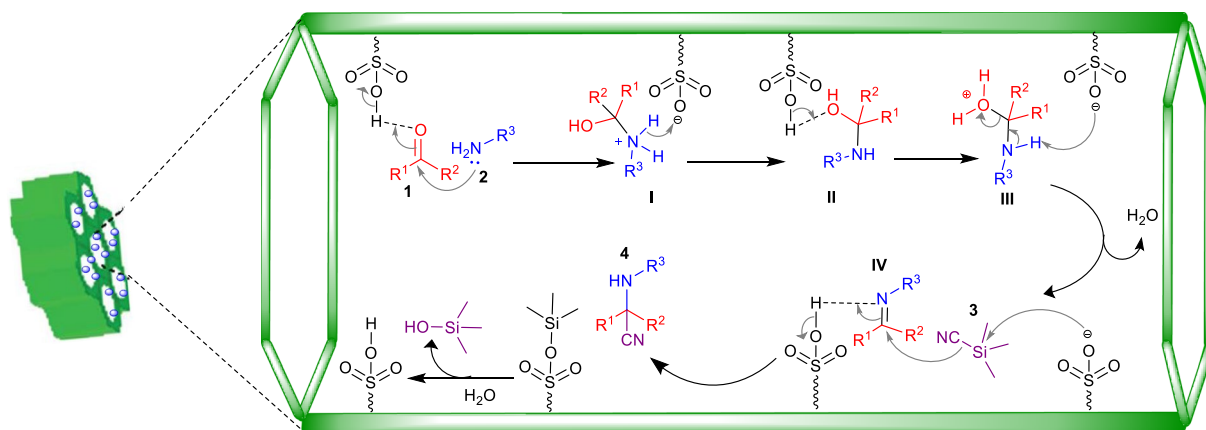
electron-withdrawing groups in the *ortho*, *meta* and *para* positions are used to react with aniline. Yields of the products are good to excellent (Table 3, entries 1–9). Also, acid-sensitive aldehydes such as cinnamaldehyde work well without the formation of any side products and give the α -aminonitrile derivatives in 90% yield (Table 3, entry 4). Different types of amines such as 4-bromoaniline, 4-chloroaniline, *p*-toluidine, benzyl amine and secondary amine such as morpholine are used in one-pot three-component condensation reactions with very good yields (Table 3, entries 10–16). Next, we direct our attention to use some ketones as carbonyl components. Pleasantly, it is found that the reactions of acetophenone, acetone and cyclohexanone with aniline and TMSCN are very efficient and the corresponding α -aminonitriles are obtained rapidly in quantitative yields (Table 3, entries 17–19). On the other hand, benzophenone is found to be unreactive under same conditions, and no product formation is detected (Table 3, entry 20).

A plausible mechanism is described for the synthesis of α -aminonitriles in the presence of MSNs-HPZ-SO₃H (Scheme 3). According to this mechanism, the catalyst active carbonyl group of aldehyde or ketone **1** through hydrogen bonding for nucleophilic attack of amine **2**. After exchange of hydrogen, intermediate (III) obtains. The removal of water from intermediate (III) produces the corresponding imine (IV), and the activated imine carbon is attacked by cyanide **3** to give product **4**.

Table 3 Synthesis of α -aminonitriles in the presence of MSNs-HPZ-SO₃H under solvent-free conditions

Entry	Aldehyde/ketone	Amine	Time (min)	Yield (%) ^a	TON	TOF (min ⁻¹)	M.p (°C)	M.p (°C) [Ref.]
1	C ₆ H ₅ CHO	C ₆ H ₅ NH ₂	10	92	46.0	4.60	78–80	80–82 [39]
2	4-ClC ₆ H ₄ CHO	C ₆ H ₅ NH ₂	10	93	46.5	4.65	112–113	109–112 [33]
3	4-MeC ₆ H ₄ CHO	C ₆ H ₅ NH ₂	15	95	47.5	3.16	77–80	76–78 [33]
4	C ₆ H ₄ CH=CHCHO	C ₆ H ₅ NH ₂	10	90	45.0	4.50	117–119	117–119 [39]
5	4-OMeC ₆ H ₄ CHO	C ₆ H ₅ NH ₂	20	92	46.0	2.30	95–96	94–96 [40]
6	2-OH-5-BrC ₆ H ₃ CHO	C ₆ H ₅ NH ₂	20	91	45.5	2.27	109–111	–
7	3-OHC ₆ H ₄ CHO	C ₆ H ₅ NH ₂	25	89	44.5	1.78	Oil	Oil [39]
8	4-OHC ₆ H ₄ CHO	C ₆ H ₅ NH ₂	20	88	44.0	2.20	122–124	121–122 [40]
9	2-ClC ₆ H ₄ CHO	C ₆ H ₅ NH ₂	15	90	45.0	3.0	68–70	67–70 [27]
10	2-ClC ₆ H ₄ CHO	4-BrC ₆ H ₄ NH ₂	30	80	40	1.33	112–114	112–116 [39]
11	C ₆ H ₅ CHO	4-ClC ₆ H ₄ NH ₂	15	90	45.0	3.0	107–108	106–108 [40]
12	C ₆ H ₅ CHO	4-MeC ₆ H ₄ NH ₂	10	92	46	4.6	105–106	107–109 [27]
13	4-MeC ₆ H ₄ CHO	4-MeC ₆ H ₄ NH ₂	15	93	46.5	3.1	107–108	104–106 [27]
14	4-ClC ₆ H ₄ CHO	4-MeC ₆ H ₄ NH ₂	10	90	45	4.5	88–91	87–90 [39]
15	C ₆ H ₅ CHO	C ₆ H ₅ CH ₂ NH ₂	20	85	42.5	2.12	Oil	Oil [33]
16	C ₆ H ₅ CHO	Morpholine	25	85	42.5	1.7	65–66	68–69 [41]
17	C ₆ H ₅ COCH ₃	C ₆ H ₅ NH ₂	30	85	42.5	1.41	148–150	150–151 [39]
18	CH ₃ COCH ₃	C ₆ H ₅ NH ₂	15	82	41	2.73	89–91	[42]
19	Cyclohexanone	C ₆ H ₅ NH ₂	10	84	42	4.2	68–70	69–71 [39]
20	Benzophenone	C ₆ H ₅ NH ₂	60	No reaction	–	–	–	–

^aIsolated yields



Scheme 3 Plausible mechanism for the synthesis of α -aminonitriles using MSNs-HPZ-SO₃H

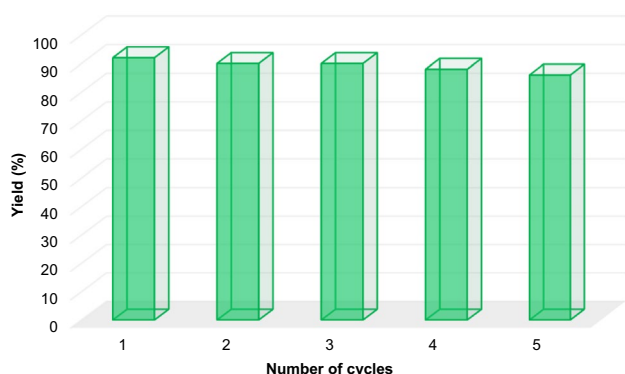


Fig. 1 Reusability of MSNs-HPZ-SO₃H in the model reaction

The possibility of recycling the catalyst MSNs-HPZ-SO₃H is also evaluated in the model reaction. Upon completion, hot ethanol is added to the reaction mixture, and the catalyst is filtered and washed with ethanol several times, dried and reused for the subsequent run. This procedure is repeated five times. The results indicate that catalyst activity changes only slightly after five catalytic cycles (Fig. 1). Also, an SEM image of the recovered catalyst after five runs is also taken, and there is no obvious change in the

morphology and size of the recovered catalyst in comparison with fresh catalyst (Fig S6, Supporting Information).

To further evaluate the overall utility of the current methodology, the catalytic activity of MSNs-HPZ-SO₃H in synthesis of α -aminonitriles is compared with several previously reported methods (Table 4). It is clear that the present method reduces the reaction time and provides a higher yield of the product.

Experimental

Materials and methods

Chemical reagents in high purity are purchased from Merck and Aldrich. Melting points are determined in open capillaries using an Electrothermal 9100 apparatus and uncorrected. Fourier transform infrared (FT-IR) spectra are recorded using KBr pellets in the range 400–4000 cm⁻¹ on a Nicolet IR-100 infrared spectrometer. The NMR spectra are recorded using a Bruker DRX 500-Avance spectrometer operating at 500 MHz for ¹H NMR in CDCl₃ with TMS as an internal standard. X-ray diffraction (XRD) is performed using Philips XPert (1710 diffractometer). The latter appears

Table 4 Comparison of catalytic activity of MSNs-HPZ-SO₃H with other known catalysts in running the model reaction

Entry	Catalyst	Conditions	Time	Yield (%)	[Ref.]
1	NHC–amide Pd(II) complex	CH ₂ Cl ₂ , rt	24 h	79	[23]
2	SO ₄ ²⁻ /ZrO ₂	THF, rt	90 min	93	[18]
3	SiO ₂	Ball milling, 700 rpm	3 h	96	[43]
4	PEG-OSO ₃ H	Water, rt	10 min	91	[31]
5	Fe ₃ O ₄ @ZrO ₂ /SO ₄ ²⁻	EtOH, rt	30 min	95	[39]
6	Nafion-H	CH ₂ Cl ₂ , 60 °C	6 h	80	[42]
7	Fe ₃ O ₄ @SiO ₂ @Me&Et-PhSO ₃ H	Solvent-free, rt	13 min	95	[44]
8	MSNs-HPZ-SO ₃ H	Solvent-free, rt	10 min	92	Present work

with Co K α ($\alpha = 1.79285$ Å) one voltage of 40 kV. Thermogravimetric/differential thermal analyses (TGA/DTA) are done on a thermal analyzer with a heating rate of 10 °C min⁻¹ over a temperature range of 25–800 °C. The particle morphology is examined by scanning electron microscopy using SEM (HITACHI S-4160), on gold-coated samples.

General procedure for preparation of the MSNs

The MSNs is synthesized according to the sol–gel method [38]. Specifically, 0.5 g of the CTAB and 0.14 g of NaOH are mixed in 240 mL deionized water. The solution is stirred vigorously at 80 °C for 2 h, then 2.5 mL of tetraethyl orthosilicate (TEOS) is added, and the reaction is continued for another 2 h. The as-prepared product (MSNs-CTAB) is washed three times with ethanol and re-dispersed in 200 mL of ethanol containing 2 g of NH₄NO₃, at 80 °C. The remaining mixture is refluxed for 6 h. Then, the resulting precipitate is centrifuged and washed with ethanol repeatedly to give a white powder which is dried under vacuum.

General procedure for preparation of the MSNs-Cl

The MSNs-Cl is prepared by refluxing 0.5 g of MSNs with 0.5 g of 3-chloropropyltrimethoxysilane (CPTMS) in toluene, under a nitrogen atmosphere, for 24 h. The resulting solid is filtered, washed with toluene and then dried under vacuum.

General procedure for preparation of the MSNs-HPZ

A solution of 1 g (10 mmol) of homopiperazine, in dry toluene and propyl amine, is added dropwise to a suspension of 0.5 g of the MSNs-Cl in toluene. This mixture is refluxed for 24 h under a nitrogen atmosphere. Then, the solid is filtered and washed in Soxhlet. After this treatment, the MSNs-HPZ powder is dried under vacuum.

General procedure for preparation of the MSNs-HPZ-SO₃H

To a solution of MSNs-HPZ (0.5 g) in *n*-hexane (2 mL), Et₃N (0.1 mL) is added. After 5 min, chlorosulfonic acid (0.1 mL) is added to the mixture and stirred for 3 h. Finally, the residue is filtered and washed with toluene, ethanol and water and dried under vacuum.

Acidity of MSNs-HPZ-SO₃H

Titration is done to determine the acid loading of the catalysts. At first, 100 mg of MSNs-HPZ-SO₃H is dispersed in 20 mL H₂O by sonicating for 40 min at room temperature after which the pH of solution becomes acidic; two drops

of phenolphthalein indicator solution is added. The acidic solution is titrated to neutrality using 0.1 M NaOH solution to determine the loading of acid sites on the MSNs-HPZ-SO₃H catalyst. The results reveal that samples of MSNs-HPZ-SO₃H possess 2 mmol H⁺ g⁻¹. This process is repeated for recovered catalyst; after reaction, the results show no substantial change in amount of acid loading of catalyst. Hence, no leaching of the acid occurred during the course of the reaction.

General procedure for preparation of α -aminonitrile

The catalyst (10 mg) is added to a mixture of aldehyde (or ketone) (1 mmol), amine (1 mmol) and TMSCN (1.2 mmol). The mixture is stirred at ambient temperature for the appropriate time. After completion of the reaction (monitored by TLC), the reaction mixture is diluted with hot ethanol and stirred for 5 min. The catalyst is removed by centrifugation or filtration. The solution is evaporated to afford the product which is recrystallized from ethanol.

Spectral data of the selected products

2-(*p*-tolyl)-2-(*p*-tolylamino)acetonitrile (Table 3, Entry 13) ¹H NMR (500 MHz, CDCl₃): δ_{H} (ppm) = 2.30 (3H, s, CH₃), 2.40 (3H, s, CH₃), 5.37 (1H, s, CH), 6.72 (2H, d, $J = 5.0$ Hz, H-Ar), 7.09 (2H, d, $J = 5.0$ Hz, H-Ar), 7.27 (2H, d, $J = 5.0$ Hz, H-Ar), 7.49 (2H, d, $J = 5.0$ Hz, H-Ar); ¹³C NMR (125 MHz, CDCl₃): δ_{C} (ppm) = 20.6, 50.5, 114.7, 118.4, 126.7, 127.2, 127.7, 130.0, 131.0, 139.5, 142.1.

2-Methyl-2-(phenylamino)propanenitrile (Table 3, Entry 18) ¹H NMR (500 MHz, CDCl₃): δ_{H} (ppm) = 1.72 (6H, s, 2CH₃), 6.95–6.98 (3H, m, H-Ar), 7.27–7.30 (2H, m, H-Ar); ¹³C NMR (125 MHz, CDCl₃): δ_{C} (ppm) = 28.2, 49.2, 117.7, 121.0, 122.0, 129.3, 143.5.

Conclusions

In this work, acid functionalized mesoporous silica nanoparticles (MSNs-HPZ-SO₃H) is synthesized and fully characterized; because of good surface area and acidity, this catalyst can be utilized efficiently for synthesis of α -aminonitriles via three-component coupling reactions of aldehydes (or ketones), amines and trimethylsilyl cyanide. The corresponding products are obtained in high yields. This protocol is a useful and attractive process for Strecker reaction due to several advantages, such as the simple experiment, short reaction times, excellent yields of products and recyclable catalyst.

Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest.

References

1. L. Banfi, G. Guanti, R. Riva, *Chem. Commun.* **11**, 985 (2000)
2. W.L. Matier, D.A. Owens, W.T. Comer, D. Deitchman, H.C. Ferguson, R.J. Seidehamel, J.R. Young, *J. Med. Chem.* **16**, 901 (1973)
3. J. Marco, S.T. Ingate, P. Manzano, *Tetrahedron Lett.* **39**, 4123 (1998)
4. S. Velázquez, C. Chamorro, M.-J. Pérez-Pérez, R. Alvarez, M.-L. Jimeno, A. Martín-Domenech, C. Pérez, F. Gago, E. De Clercq, J. Balzarini, *J. Med. Chem.* **41**, 4636 (1998)
5. D. Enders, J.P. Shilvock, *Chem. Soc. Rev.* **29**, 359 (2000)
6. R.O. Duthaler, *Tetrahedron* **50**, 1539 (1994)
7. S.J. Zuend, M.P. Coughlin, M.P. Lalonde, E.N. Jacobsen, *Nature* **461**, 968 (2009)
8. L.M. Weinstock, P. Davis, B. Handelsman, R.J. Tull, *J. Org. Chem.* **32**, 2823 (1967)
9. A. Strecker, *Liebigs Ann. Chem.* **75**, 27 (1850)
10. B.A.B. Prasad, A. Bisai, V.K. Singh, *Tetrahedron Lett.* **45**, 9565 (2004)
11. S.K. De, R.A. Gibbs, *J. Mol. Catal. A: Chem.* **232**, 123 (2005)
12. S. Kobayashi, T. Busujima, *Chem. Commun.* **9**, 981 (1998)
13. S.K. De, *J. Mol. Catal. A: Chem.* **225**, 169 (2005)
14. Z.-L. Shen, S.-J. Ji, T.-P. Loh, *Tetrahedron* **64**, 8159 (2008)
15. A. Majhi, S.S. Kim, S.T. Kadam, *Tetrahedron* **64**, 5509 (2008)
16. M. Narasimhulu, T.S. Reddy, K.C. Mahesh, S.M. Reddy, A.V. Reddy, Y. Venkateswarlu, *J. Mol. Catal. A: Chem.* **264**, 288 (2007)
17. B. Karimi, A.A. Safari, *J. Organomet. Chem.* **693**, 2967 (2008)
18. B.M. Reddy, B. Thirupathi, M.K. Patil, *J. Mol. Catal. A: Chem.* **307**, 154 (2009)
19. J.S. Yadav, B.V.S. Reddy, B. Eshwaraiah, M. Srinivas, P. Vishnumurthy, *New J. Chem.* **27**, 462 (2003)
20. M.Z. Kassaei, H. Masrouri, F. Movahedi, *Appl. Catal. A Gen.* **395**, 28 (2011)
21. S. Bagheri, M.A. Zolfigol, R. Schirhagl, M. Hasani, M.C.A. Stuart, A. Nagl, *Appl. Organomet. Chem.* **31**, e3883 (2017)
22. B. Karimi, D. Zareyee, *J. Mater. Chem.* **19**, 8665 (2009)
23. J. Jarusiewicz, Y. Choe, K.S. Yoo, C.P. Park, K.W. Jung, *J. Org. Chem.* **74**, 2873 (2009)
24. K. Iwanami, H. Seo, J.-C. Choi, T. Sakakura, H. Yasuda, *Tetrahedron* **66**, 1898 (2010)
25. A. Heydari, A. Arefi, S. Khaksar, R.K. Shiroodi, *J. Mol. Catal. A: Chem.* **271**, 142 (2007)
26. B. Karmakar, J. Banerji, *Tetrahedron Lett.* **51**, 2748 (2010)
27. M.G. Dekamin, M. Azimoshan, L. Ramezani, *Green Chem.* **15**, 811 (2013)
28. K. Surendra, N.S. Krishnaveni, A. Mahesh, K.R. Rao, *J. Org. Chem.* **71**, 2532 (2006)
29. J. Wang, Y. Masui, M. Onaka, *Eur. J. Org. Chem.* **2010**, 1763 (2010)
30. F. Rajabi, S. Nourian, S. Ghiassian, A.M. Balu, M.R. Saidi, J.C. Serrano-Ruiz, R. Luque, *Green Chem.* **13**, 3282 (2011)
31. M. Shekouhy, *Catal. Sci. Technol.* **2**, 1010 (2012)
32. S. Bagheri, M.A. Zolfigol, M. Safaiee, D.A. Alonso, A. Khoshnood, *Appl. Organomet. Chem.* **31**, e3775 (2017)
33. J.S. Yadav, B.V.S. Reddy, B. Eshwaraiah, M. Srinivas, *Tetrahedron* **60**, 1767 (2004)
34. A. Dutta, J. Mondal, A.K. Patra, A. Bhaumik, *Chem. Eur. J.* **18**, 13372 (2012)
35. K. Ghosh, R.A. Molla, M.A. Iqbal, S.M. Islam, *Green Chem.* **17**, 3540 (2015)
36. M. Hajjani, F. Ghorbani, F. Bakhti, *Appl. Catal. A Gen.* **470**, 303 (2014)
37. Z. Nasresfahani, M.Z. Kassaei, E. Eidi, *New J. Chem.* **40**, 4720 (2016)
38. I.I. Slowing, B.G. Trewyn, V.S.-Y. Lin, *J. Am. Chem. Soc.* **129**, 8845 (2007)
39. H. Ghafari, A. Rashidizadeh, B. Ghorbani, M. Talebi, *New J. Chem.* **39**, 4821 (2015)
40. H. Singh, J.K. Rajput, P. Arora, *RSC Adv.* **6**, 84658 (2016)
41. B.C. Ranu, S.S. Dey, A. Hajra, *Tetrahedron* **58**, 2529 (2002)
42. G.K.S. Prakash, E. Thomas, I. Bychinskaya, A.G. Prakash, C. Panja, G.A. Olah, *Green Chem.* **10**, 1105 (2008)
43. J.G. Hernández, M. Turberg, I. Schiffrers, C. Bolm, *Chem. Eur. J.* **22**, 14513 (2016)
44. A. Mobaraki, B. Movassagh, B. Karimi, *ACS Comb. Sci.* **16**, 352 (2014)

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