



Application of Sulfonic Acid Functionalized Nanoporous Silica (SBA-Pr-SO₃H) in the Green Strecker Reaction under Solvent Free Condition

¹Ghodsi Mohammadi Ziarani,² Alireza Badiei,
¹Masoomeh Azizi, ¹Parisa Gholamzadeh and ¹Leila Seyedakbari

¹Department of Chemistry, Alzahra University,
Vanak Square, P.O. Box 1993893973, Tehran, Iran

²School of Chemistry, College of Science,
University of Tehran, P.O. Box 14155-6455, Tehran, Iran

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Abstract: An efficient green and benign synthesis was developed in the one-pot three component Strecker reaction using heterogeneous nanoporous acid catalyst of SBA-Pr-SO₃H with a pore size of 6 nm under solvent free condition. This method has the advantages of short reaction time, ease of the products isolation, excellent yields for the products.

Key words: SBA-Pr-SO₃H • Strecker reaction • Green synthesis • Multi component reaction

INTRODUCTION

Amino acids are an important group of natural products which have different roles in human life. Twenty types of α -amino acids make all of the proteins around of us. α -Aminonitriles (**1**) are the useful intermediates to synthesis of α -amino acids. For the first time, Strecker synthesized alanine which is one of the amino acids widely occurring in proteins in 1850 [1]. Nowadays, Strecker reaction has the most application to large-scale production of α -amino acids due to the ready availability of its starting materials. Through the years, Strecker reaction have been developed using various cyanide sources such as HCN [2], KCN [3], (EtO)₂ P(O)CN [4], Et₂AlCN [3], Bu₃SnCN [5] and TMSCN [6]. Different catalysts have been used in Strecker reaction such as Cu(OTf)₂ [6], InCl₃ [7], NH₂SO₃H [8], K₅CoW₁₂O₄₀ · 3H₂O [9], XSA [10] and tin ion exchanged montmorillonite [11]. One of the most important concepts in chemistry is green chemistry which is based on elimination of hazardous substances in the synthetic processes. For this purpose, the solvents is removed from the reaction and heterogeneous catalyst based on silicon is used in the green synthesis [12].

Mesoporous silica SBA-15 was synthesized for the first time in 1998 by Zhao and coworkers [13, 14]. These materials have attracted vast interest because of their potential applications as catalyst support [15], adsorbents as well as nanoreactors for making an ordered crystalline alumina molecular sieves [16, 17]. SBA-15 is a nanoporous silica with a hexagonal structure, excellent stability (chemical and thermal), good accessibility due to high surface areas, large pore size, high selectivity and isolation ease of the products [18, 19]. Sulfonic acid functionalized nanoporous silica (SBA-Pr-SO₃H) as a green and heterogeneous nano catalyst with noncorrosive properties was prepared by the functionalization of SBA-15 [20, 21]. We have used this nano acid catalyst (SBA-Pr-SO₃H) in multi component reactions [22-26]. In continuation of our work, we have decided to use it in the Strecker reaction.

MATERIALS AND METHODS

The chemicals employed in this work were obtained from Merck Company and were used with no purifications. IR spectra were recorded from KBr disk using a FT-IR Bruker Tensor 27 instrument.

Melting points were measured by using the capillary tube method with an electro thermal 9200 apparatus. The ¹H NMR (250 MHz) was run on a Bruker DPX using TMS as an internal standard. GC-Mass analysis was performed on a GC-Mass model: 5973 network mass selective detector, GC 6890 Agilent. SEM analysis was performed on a Philips XL-30 field-emission scanning electron microscope operated at 16 kV while TEM was carried out on a Tecnai G² F30 at 300 kV.

Synthesis and Functionalization of SBA-15: The nanoporous compound SBA-15 was synthesized and functionalized according to our previous report [24] and the modified SBA-15-Pr-SO₃H was used as nanoporous solid acid catalyst in the following reaction.

General Procedure for the Preparation of α-aminonitrile Derivatives: The SBA-Pr-SO₃H was activated in vacuum at 100°C and then after cooling of catalyst to room temperature, aryl aldehydes (1 mmol), amine (1.2 mmol) and TMSCN (1.5 mmol, 0.148 g) were added to it. The mixture was stirred in appropriate time as shown in Table 2. After completion of the reaction which monitored by TLC, the crude product was dissolved in hot dichloromethane and then filtered for removing the solid catalyst. Filtrate was cooled to give the pure product. The solid acid catalyst subsequently was washed with diluted acid solution, distilled water and then acetone, dried under vacuum and then it can be used for several times without loss of significant activity.

2-(N-Anilino)-2-(4-chlorophenyl) acetonitrile (1c): IR (KBr): ν_{\max} = 3300, 3095, 3055, 3024, 2246, 1600, 1517, 1491, 1401, 1273, 1090, 1009, 813, 754 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz): δ = 4.05 (br s, 1H), 5.41 (s, 1H), 6.75 (d, J= 7.75 Hz, 2H), 6.91 (t, J= 7.5 Hz, 1H), 7.24-7.30 (m, 2H), 7.41 (d, J= 7.5 Hz, 2H), 7.47 (d, J= 7.5 Hz, 2H) ppm. MS (m/e): 242 [M⁺], 214, 150, 112, 92, 77.

2-(N-Anilino)-2-(4-methylphenyl) acetonitrile (1d): IR (KBr): ν_{\max} = 3308, 3105, 3026, 2950, 2243, 1600, 1516, 1459, 1243, 1114, 888, 755 cm⁻¹. ¹H NMR (CDCl₃,

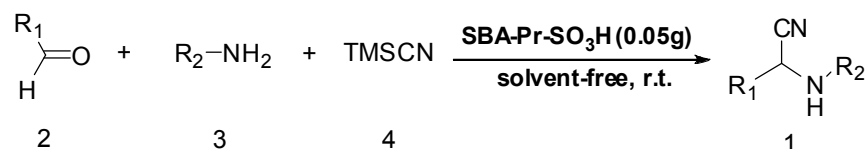
250 MHz): δ = 2.39 (s, 3H), 4.0 (br s, 1H), 5.37 (s, 1H), 6.77 (d, J= 7.5 Hz, 2H), 6.89 (t, J= 7.5 Hz, 1H), 7.24-7.30 (m, 4H), 7.47 (d, J= 7.5 Hz, 2H) ppm. MS (m/e): 222 [M⁺], 196, 169, 130, 91, 77.

2-(N-Anilino)-2-(4-methoxyphenyl) acetonitrile (1f): IR (KBr): ν_{\max} = 3327, 3009, 2933, 2227, 1602, 1508, 1270, 1240, 1176, 1021, 826, 756 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz): δ = 3.83(s, 3H), 4.00 (d, J= 7.5 Hz, 1H), 5.35 (s, 1H), 6.76 (d, J= 7.5 Hz, 2H), 6.79-6.97 (m, 3H), 7.24- 7.30 (m, 2H), 7.49 (d, J= 7.5Hz, 2H) ppm. MS (m/e): 238 [M⁺], 212, 146, 131, 92, 77.

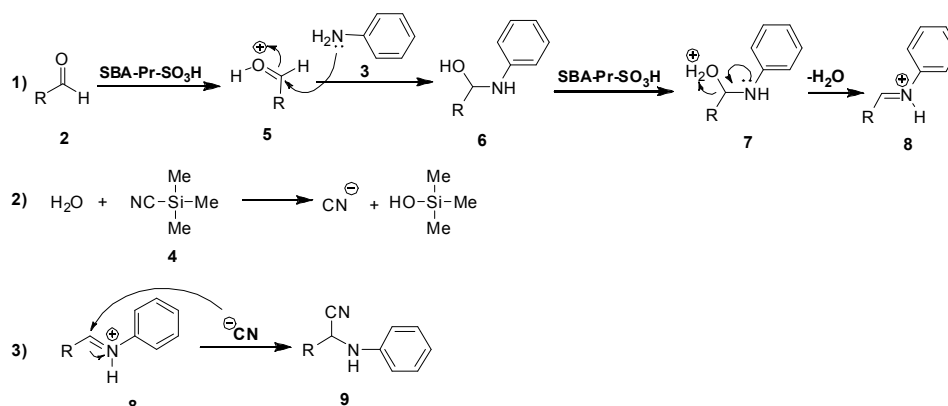
2-(N-Anilino)-2-(3-methylphenyl) acetonitrile (1g): IR (KBr): ν_{\max} = 3346, 3028, 2924, 2235, 1599, 1513, 1307, 1244, 1093, 751 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz): δ = 2.39 (s, 3H), 4.01 (br s, 1H), 5.36 (s, 1H), 6.76 (d, J= 7.75 Hz, 2H), 6.89 (t, J= 7.5 Hz, 1H), 7.22 (s, 1H), 7.23-7.4 (m, 5H) ppm. MS (m/e): 222 [M⁺], 196, 169, 130, 91, 77.

RESULT AND DISCUSSION

In this paper, the Strecker reaction of aromatic aldehydes (**2**), amine (**3**) and trimethylsilyl cyanide (**4**) in the presence of nanoporous solid acid catalyst (SBA-Pr-SO₃H) has been studied (Scheme 1). As shown results in Table 1, among the tested solvents such as CH₃CN, CH₂Cl₂, MeOH, H₂O and solvent free system, the best results were obtained after 5 min in the solvent free condition in excellent yield. The high yields of reactions are related to the effect of a nanopore size about 6 nm of solid acid catalyst which acts as nano-reactor (Figure 1). Therefore, this reaction was performed with different aldehydes and the results were summarized in the Table 2. The reaction time was 5-10 min and excellent yields of the products were obtained. The acid catalyst was separated from the crude products and reactivated by simple washing subsequently with diluted acid solution, water and acetone and then reused without noticeable loss of reactivity. Some known products were characterized by IR and ¹H NMR spectroscopy data. Melting points are compared with reported values in the literature as shown in Table 2.



Scheme 1: Synthesis of α-aminonitriles using Strecker reaction by SBA-Pr-SO₃H.



Scheme 2: Suggested mechanism for the SBA-Pr-SO₃H catalyzed Strecker reaction.

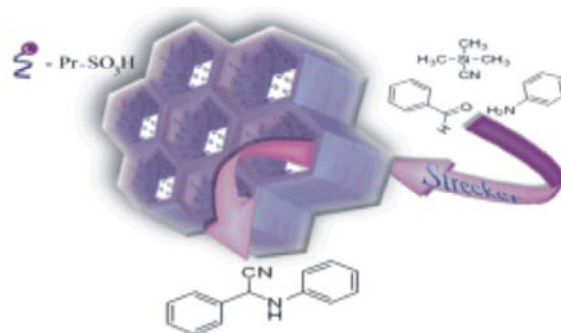


Fig. 1: SBA-Pr-SO₃H acts as a nano-reactor.



Fig. 2: Schematic illustration for the preparation of SBA-Pr-SO₃H.

Table 1: The optimization of Strecker reaction conditions in the synthesis of 2-(N-Anilino)-2-(phenyl)acetonitrile at room temperature (1a).

Entry	Solvent	Time (h)	Yield (%)
1	CH ₃ CN	0.5	92
2	CH ₂ Cl ₂	1	85
2	H ₂ O	1.5	88
3	CH ₃ OH	2.5	78
4	Solvent free	5 min	98

The suggested mechanism for the SBA-Pr-SO₃H catalyzed Strecker reaction was shown in Scheme 2. Concerning the reaction mechanism, we suggest that initially, the solid acid catalyst protonates the carbonyl group of aldehyde (2) followed by nucleophilic attack of

aniline (3) to carbonyl carbon to give the product adduct (6) which is protonated and dehydrated to give an iminium ion (8) in the presence of solid nano acid catalyst. Trimethylsilyl cyanide (4) is hydrolyzed to give cyanide ion intermediate which attacks to the iminium carbon yielding an α -aminonitrile.

The Strecker reaction has been studied in several conditions in literature as shown in Table 3. In comparison with other existing methods, the present methodology has several advantages such as a greener conditions, short reaction time, easy work-up, non-corrosiveness catalyst and excellent yields with high purity of products.

Table 2: SBA-Pr-SO₃H catalyzed the Strecker reaction under solvent free condition.



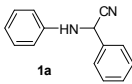


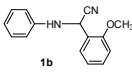


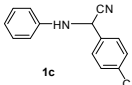


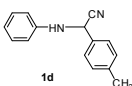


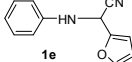


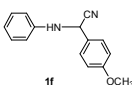


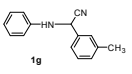


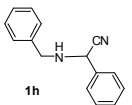


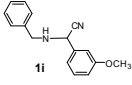


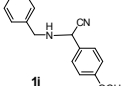
Entry	Aldehyde	Amine	Product	Time (min)	Yield (%)	mp (°C)	mp (Lit)
1				5	98	73-74	74-75 [27]
2				6	98	65-67	61-62 [28]
3				10	96	111-119	108-110 [27]
4				6	97	75-76	74-76 [27]
5				5	98	67-68	67-69 [29]
6				5	98	92-94	92-94 [27]
7				7	97	89-91	98-99 [30]
8				5	98	Colorless oil	30-32 [31]
9				8	95	Colorless oil	Colorless oil [10]
10				7	95	Yellow oil	Yellow oil [29]

Table 3: Comparison of different condition in the 2-(N-anilino)-2-phenylacetone nitrile.

Entry	Catalyst	Condition	Time	Yield (%)	Year
1	SBA-Pr-SO ₃ H	Neat, rt.	5 min	98	This work
2	GA-TUD-1	Neat, rt.	0.5 h	95	2011 [27]
3	SO ₄ ²⁻ /ZrO ₂	THF, N ₂ , rt.	90 min	93	2009 [32]
4	XSA	MeCN, rt.	65 min	97	2009 [10]
5	TFE	neat, rt.	2 h	97	2009 [33]
6	InI ₃	H ₂ O, rt.	0.5 h	95	2008 [34]
7	H ₂ SO ₄ /Silicagel	MeCN, rt.	60 min	93	2008 [35]
8	Fe(Cp) ₂ PF ₆	neat, rt.	20 min	94	2008 [36]
9	NH ₂ SO ₃ H	neat, rt.	5 min	98	2007 [8]
10	K ₅ CoW ₁₂ O ₄₀ .3H ₂ O	MeCN, rt.	50 min	95	2007 [9]

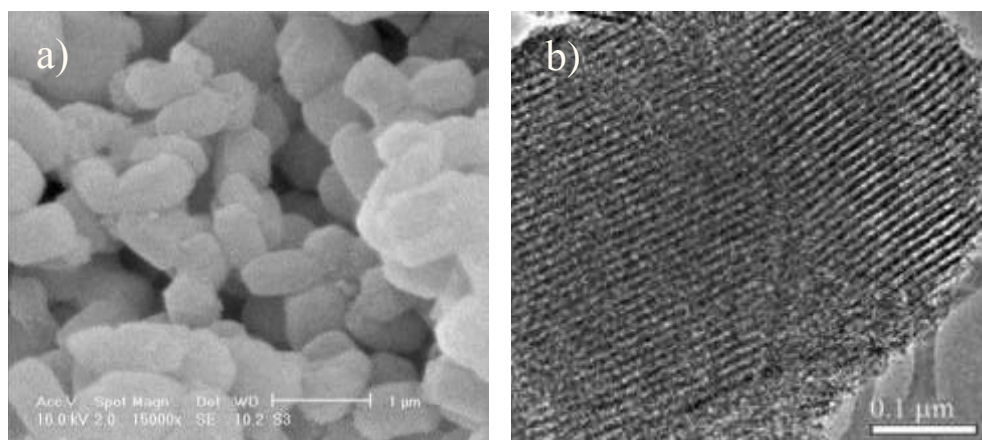


Fig 3: SEM (a) and TEM (b) image of SBA₃Pr-SO₃H.

Preparation of Catalyst: New nanoporous silica SBA-15 can be obtained by using commercially available triblock copolymer Pluronic P126 as a structure directing agent [13, 14]. Functionalizing of SBA-15 with -SO₃H group was usually performed through direct synthesis or post-grafting. As shown in Figure 2, the SBA-15 silica was functionalized with (3-mercaptopropyl) trimethoxysilane (MPTS) and then the thiol groups of the product were oxidized to sulfonic acid by hydrogen peroxide. Analyzing of the catalyst surface was performed by various methods such as TGA, BET and CHN methods which demonstrated that the propyl sulfonic acids were immobilized into the pores. Calculating average pore diameter of the surface area was performed by the BET method and pore volume of SBA-Pr-SO₃H is 440 m²g⁻¹, 6.0 nm and 0.660 cm³g⁻¹, respectively, which are smaller than those of SBA-15 due to the immobilization of sulfonosilane groups into the pores [24]. SEM image of SBA-Pr-SO₃H (Fig. 3 left) shows uniform particles about 1 μm. The same morphology was observed for SBA-15. It can be concluded that morphology of solid was saved without change during the surface modifications. On the other hand, the TEM image (Fig. 3 right) reveals the parallel channels, which resemble the pores configuration of SBA-15. This indicates that the pore of SBA-Pr-SO₃H was not collapsed during two steps reactions.

In conclusion, we reported a novel and highly efficient method for the Strecker reaction that has been developed in the solvent free reaction of aromatic aldehydes, amines and TMSCN using recyclable and environmentally benign Sulfonic acid functionalized nanoporous silica (SBA-Pr-SO₃H).

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