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An Efficient One-Pot Green Approach for the Synthesis of A-aminonitriles with Alsba-15 as Nano Tubular Catalytic Reactor

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Nanoporous heterogeneous AlSBA-15 (*x*) type aluminosilicate catalyst with different n_{Si}/n_{Al} ratios (x = 41, 129, and 210) was synthesized using hydrothermal method. AlSBA-15 catalysts were characterized by XRD, N_2 sorption, TPD-NH_3, FT-IR, SEM and TEM. XRD analyses of AlSBA-15 catalysts confirmed the presence of well-ordered crystalline structure with *p6mm* symmetry. N_2 isotherm of AlSBA-15 catalyst materials showed a type IV adsorption isotherm with H1 hysteresis loops. The specific surface area and specific pore volume of the AlSBA-15 catalysts are in the rage from 480 to 757 m^2/g and from 0.65 to 0.95 cm^3/g, respectively. SEM analysis of AlSBA-15 (41) revealed a worm-like particle morphology comprising particles in a size range of 3 μm with the co-existence of smaller particles of *ca.* 1 μm size. A distinct approach adopted for the synthesis of α-aminonitriles using heterogeneous nanoporous AlSBA-15 catalyst via Strecker reaction. This one-pot, three component system of amines (primary/secondary), carbonyl compounds (aldehydes/ketone) and TMSCN compounds proceed excellently in the presence of AlSBA-15 catalyst in water medium at room temperature (RT). The major advantages are excellent yield, short reaction time, high chemo-selectivity, simple experimental procedure, recyclability of the catalyst, easy work up procedure. This one-pot synthesis consists of two consecutive steps: (1) imine formation from amine and aldehyde/ketone and (2) cyano addition to imine. The findings suggest that catalyst is recyclable and can be reused up to six cycles.

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INTRODUCTION

α-Aminonitriles are having remarkable immense biological activities[1] such as anticancer, antibacterial, antifungal, antiviral and antibiotic. They are used as starting materials and/or intermediates in organic synthesis and medicinal chemistry to synthesis a variety of very important compounds like amino acids [2], amides [3], diamines [4], imidazoles [5], thiadiazoles [6], and antitumor agents like saframycin-A and phthalascidin [7]. α-Aminonitriles are essential building blocks in peptide and protein synthesis. Strecker reaction employs carbonyl and amine compounds are treated with metal cyanides (NaCN and KCN). But handling of metal cyanides in large scale production as well as in work-up stage found great difficulties due to its toxicity. To overcome these difficulties, many efforts have been taken and employed number of alternative cyanide sources for this reaction till now. Trimethylsilyl cyanide (TMSCN) [8-12] was found very effective, easy to handle, relatively safe cyanation source when compared to the metal cyanides [13-18]. In Strecker reaction transfer of cyanide ion or CN^- is facilitated in presence of Lewis and Brønsted acid catalysts. Several researchers have been employed different Lewis and Brønsted acid catalysts such as $Yb(OTf)_3$ [19], $Cu(OTf)_2$ [20], $BiCl_3$ [21], $RuCl_3$ [22], $Sc(OTf)_3$ [23], K_2PdCl_4 [24], $GdCl_3.6H_2O$ [25], InI_3 [26], $CeCl_3$ [27], $ZrCl_4$ [28], $K_4[Fe(CN)_6]$ [29], and *p*-toluenesulfonic acid [30] for the synthesis of α-aminonitriles. But most of them suffer from at least one of the following disadvantages: harsh reaction conditions, air sensitivity, the use of stoichiometric, toxic nature and relatively expensive reagents or catalysts, poor product yield, long reaction time and tedious separation procedure. Moreover, these catalysts are not recyclable and reusable in organic solvents. To compensate these deficiencies, numerous endeavours have been made, giving rise to satisfactory results in terms of efficiency and rate of the reaction, but still two major problems addressed. (1) The use of a metal or metal complex as catalyst which is poisoning the environment and remains as an impurity in the final product and (2) The matter of recycling and reusability of the catalyst.

The nanoporous AlSBA-15 possess a large surface area (~700 m^2/g), uniform narrow pore size distribution ranging from 4.5 to 15 nm having considerable thicker pore wall (3 to 6 nm) and thus exhibits higher thermal and hydrothermal stability (800 °C), and strong Brønsted

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and Lewis acidity. All these characteristics made this material to be a potential candidate for a wide range of catalytic application as catalyst and/or catalytic support [31-33]. Few attempts have been made to perform the Strecker reaction in heterogeneous catalytic system using the catalysts such as CeO_2 [34], Fe_3O_4–BF_3 [35], $Bi(NO_3)_3\cdot 5H_2O$ [36], inorganic hybrid nanocatalyst [37], Nafion®SAC-13 [38], $CuFe_2O_4$ [39], $K_5CoW_{12}O_{40}.3H_2O$ [40], KSF-supported hetero polyacids [41], Al_2O_3-supported 12-tungstosilicic acid [42]. But these heterogeneous catalysts have poor catalytic performance due to low surface area, disordered irregular pore system which leads to the low conversion and product selectivity. In recent decades, use of water as solvent attains considerable attention in synthetic community and proved to be a promising solvent in organic synthesis due to its cost-effectiveness, environmentally friendly and polar nature [43-45]. We inspired from the previous results of Strecker reactions carried out in water medium in a three component system [46-49].

Hence, herein to the best of our knowledge for the first time we report the synthesis of α-aminonitrile *via* Strecker reaction in a three-component system of amines, aldehydes/ketones and trimethylsilyl cyanide using heterogeneous nanoporous AlSBA-15 catalyst in water medium at RT in a short reaction time. Use of this catalyst solves problem of catalyst recovery by a simple filtration and the recovered catalyst can be reused for several reaction cycles.

MATERIAL AND METHODS

Materials

AlSBA-15 materials were synthesized using tetraethylorthosilicate (TEOS, 98 % Sigma-Aldrich) and aluminium isoproxide (≥98 % Sigma-Aldrich) as silicon and Aluminium precursors, respectively. Nonionic triblock copolymer surfactant $EO_{20}PO_{70}EO_{20}$ (P123, Aldrich) was used as the structure-directing agent. Concentrated HCl aqueous solution was used as acid source. Remaining chemicals and reagents were purchased from Aldrich and were used without further purification.

Catalyst preparation

The synthesis of AlSBA-15 (x) nanoporous silica with different n_{Si}/n_{Al} ratios (x = 41, 129, and 210) was employing optimized procedure with the molar gel composition TEOS: 0.03-0.14 Al_2O_3: 0.016 P123: 0.96 HCl: 126 H_2O as described elsewhere [50]. In a typical synthesis procedure of AlSBA-15 materials, triblock copolymer of P123 stirred with deionised water to get clear solution. Thereafter, the required amount of HCl was added and stirred for another 2 h. Then required amount of tetraethyl orthosilicate and aluminium isopropoxide were added and then the resulting mixture was continuously stirred at 40 °C for 24 h, aged at 100 °C for 48 h. The crystallized product was filtered, washed, dried, and calcined at 550 °C for 36 h. The AlSBA-15 samples were designated as AlSBA-15 (x), x where denotes the n_{Si}/n_{Al} ratio.

Characterisation

XRD patterns of AlSBA-15 samples were obtained with a powder X-Ray diffractometer (Smart lab, Rigaku, Japan). Nitrogen sorption isotherms were obtained from Quantachrome Autosorb 1 sorption analyzer, USA. Scanning electron microscopy (SEM) analysis was performed using a Hitachi S-4800 instrument operating at 10 kV. Prior to the SEM analysis, the samples were placed under an E1010 ion sputtering instrument to improve their conductivity. Transmission electron microscopy (TEM) analysis was carried out using a Hitachi H-7560 electron microscope operating at an accelerating voltage of 100 kV. FT-IR measurements were performed on scientific-NICOLET IS10 (USA). The temperature-programmed desorption (TPD) of pyridine was performed on different AlSBA-15 materials. About 100 mg of the sample was evacuated for 3 h at 250 °C under vacuum ($P< 10^{-5}$ hPa). Thereafter, the sample was cooled to room temperature under dry nitrogen atmosphere. Subsequently, the sample was subjected to exposure of pyridine vapours along with nitrogen for 30 min. Physisorbed pyridine was removed by heating the sample at 120 °C for 2 h in a nitrogen flow. The TPD measurement of pyridine adsorbed sample was analyzed by high resolution thermogravimetric analyser (SETARAM setsys 16MS) at a heating rate of 10 °C/min from 120 to 600 °C under nitrogen flow (50 ml/min). The observed weight loss was used to quantify the number of acid sites, assuming that each mole of pyridine corresponds to one mole of proton. Temperature-programmed desorption of ammonia (NH_3-TPD) study of fresh and reused AlSBA-15 (41) catalyst was conducted to determine the decrease in acid sites concentration of reused AlSBA-15 catalyst. Before the adsorption of ammonia at 373K, the samples were heated to 823K in a He flow. The ammonia desorbed between 373 and 823K (heating rate of 10K min^{-1}) was analyzed by an on-line gas chromatograph (Shimadzu GC-14A) provided with a TC detector.

Thin layer chromatography (TLC) was performed using Merck 60 F_{254} precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm). Further visualization was carried out by staining with an ethanolic solution of ninhydrin. Flash-column chromatography was performed using silica gel (100-200 mesh) with commercially available solvents. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR spectra were recorded on Bruker AVANCE III, 400 and 500 MHZ spectrophotometers using TMS as an internal standard. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.2600, s). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); or m (multiplet). Coupling constants are reported as a *J* value in hertz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.03, t). FT-IR spectra were recorded on a SHIMADZU FTIR spectrometer. LCMS spectrums were recorded using the follows, Description: Agilent 1290 series, Mass 6150 quadru pole LCMS, Software: Chemistation; and LCMS run method specifications are Column: Acquity UPLC BEH C18 (50 mm x 2.1 mm, 1.7 µm), Mobile Phase: B: 0.1 % Formic acid in water, A: 0.1 % formic acid in acetonitrile, Gradient: Time (min)/% A: 0/2, 0.2/2, 1.5/98, 2.6/98, 2.61/2,3.2/2, Column Temp: 45 °C, Flow rate: 0.8 ml/min. HRMS analysis: The compound was dissolved in a solution of 50 % (v/v) HPLC grade acetonitrile (Ranchem), 50 % (v/v) deionized water and 0.1 % formic acid. The solution was auto injected simultaneously with reference sample to ESI source at a flow rate of 500 µL min^{-1}. ESI (+)-MS was acquired using a hybrid high-resolution and high accuracy (5 µL/L) microTof (Q-TOF) mass spectrometer (Waters Q-Tofmicro) under the following conditions: capillary and cone voltages were set to + 2960 V and +142 V, respectively with a de-solvation temperature of 244 °C. For data acquisition and processing in QTOF-control data analysis software (Mass Lynx) was used. The data were collected in the *m/z* range of 100–1000 at the speed of two scans per second.

General procedure for the synthesis of α-aminonitriles

Typical procedure for the one-pot synthesis of α-aminonitrile: A mixture of aldehyde compound (3 mmol), amine compound (3 mmol), TMSCN (3 mmol) and AlSBA-15 (15 mg) in water (5 ml) were stirred at RT for the appropriate reaction time (20-55 min). The reaction completion was monitored by TLC. After completion of reaction, the reaction mixture was diluted with ethyl acetate (5 ml), then filtered through Whatman filter paper and washed with ethyl acetate (2 ml). The organic layer was separated and washed with saturated brine solution (5 ml), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by washing with diethyl ether or column chromatography by using silica gel (100-200 mesh size) and eluting with ethyl acetate/hexane of increasing polarity.

RESULTS AND DISCUSSION

The powder XRD patterns of AlSBA-15 samples are shown in Figure 1. The low angle XRD patterns (a) of AlSBA-15 samples show a very intense peak due to (100) reflection at 2θ= 0.87 and weak peaks at 2θ = 0.93 and 0.96 due to (110) and (200) reflections, respectively, which indicates the persistence of *p6mm* hexagonal symmetry. It is interesting to note that the lattice parameters (*d*-spacing and a_o) of AlSBA-15 increases significantly with the increase of aluminium content in the synthesis gel (Table 1) due to the substitution of Al^{3+} with ionic radii 0.57 A^o in place of Si^{4+} having ionic radii of 0.26 A^o in the SiO_2 framework. The high angle XRD patterns (b) of AlSBA-15 samples showed a broad peak at the 2θ value of 24 due to the amorphous silica and there were no peaks due to aluminium oxide in AlSBA-15. It clearly indicates that there were no agglomerated aluminum oxide species found in AlSBA-15 samples [51-52]. The nitrogen sorption isotherms (a) and BJH pore size distribution (b) of AlSBA-15 samples are shown in Figure 2 and the textural properties are indicated in Table 1. AlSBA-15 samples exhibit type IV adsorption isotherm with H_1 hysteresis loop as defined by IUPAC indicating the presence of a cylindrical narrow pore size distribution in the catalytic materials. The specific surface area and the pore volume are gradually decreased with increase in the amount of aluminium content in the silica matrix. BJH pore size distribution of AlSBA-15 showed a narrow pore size distribution with the maximum average pore diameter at *ca.* 55 A^o [53-55].

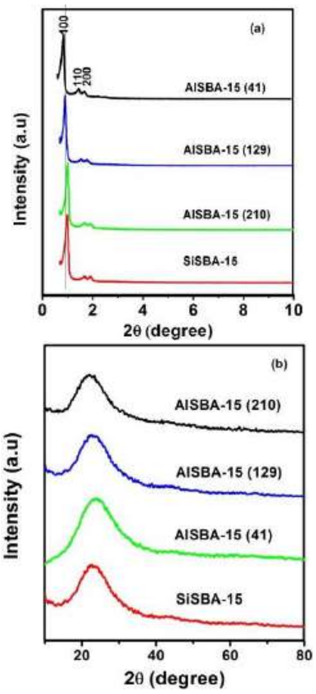


Figure 1. The XRD patterns of AlSBA-15 samples (a) Low angle and (b) High angle.

The temperature programmed desorption (TPD) of pyridine data are presented in Table 1. Three distinct weight losses were observed in the samples of AlSBA-

15, which are assumed to be the acid sites of weak (weight loss between 120 and 350 °C), moderate (351 and 450 °C) and strong (451 and 600 °C). The weak acid sites are due to surface hydroxyl group, and the medium and strong acid sites are originated from the incorporation of aluminum into the SBA-15 framework. The weak acid sites increase as the n_{Si}/n_{Al} increases. This can be attributed to the weakly held hydrogen bonded pyridine on terminal silanol group increases. However, the medium and strong acid sites decrease with increase of n_{Si}/n_{Al} ratio.

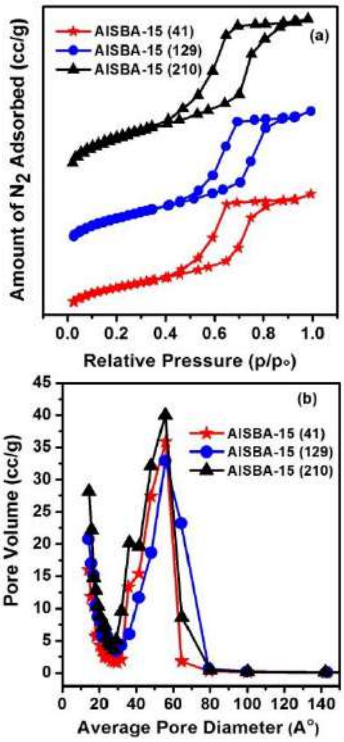


Figure 2. (a) N_2 sorption isotherms and (b) pore size distributions of AlSBA-15 samples with different *n*Si/*n*Al ratio.

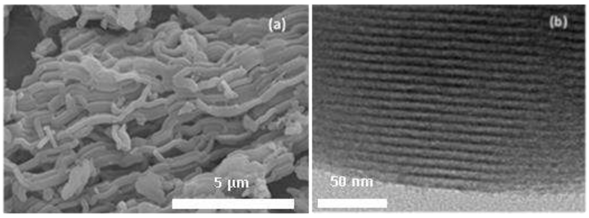


Figure 3. (a) SEM image and (b) TEM image of AlSBA-15 (41) sample.

The surface morphology of AlSBA-15 samples is studied by SEM and TEM corresponding micrographs are presented in Figure 3. Elemental compositions of AlSBA-15 samples are provided in Table 1. The n_{Si}/n_{Al} ratio of calcined AlSBA-15 catalysts is higher than the n_{Si}/n_{Al} ratio in the synthesis gel. This is due to the high solubility of aluminum isopropoxide in the acidic medium. However AlSBA-15 samples with n_{Si}/n_{Al} ratios ranging from 41 to 210 have been synthesized hydrothermally. The SEM image (a) of AlSBA-15 sample shows aggregates of warm like regular rod-shaped particles of *ca.* 3 µm size with the co-existence of smaller particles of *ca.* 1 µm size. The TEM image (b) of AlSBA-15 (41) materials shows well-ordered hexagonal arrays of nanopores with one-dimensional nano channels indicating the presence of 2D hexagonal (*p*6*mm*) symmetry. FT-IR spectra of the AlSBA-15 samples are shown in Figure 4 and 5. The predominant bands at 1088, 803, 956, 3400-3500 and 1376 cm^{-1} were found in the FT-IR spectra of AlSBA-15 samples. The bands at 1082 cm^{-1} and 798 cm^{-1} are assigned to an anti-symmetric and symmetric stretching vibration of Si-O-Si. The absorption band at 964 cm^{-1} is due to the anti-symmetric Si-O-Al vibration bands. A broad band in the range of 3400-3500 cm^{-1} due to presents of free Si-OH groups in the framework. The absorption band at 1641 cm^{-1} is due to adsorbed water molecules and the deformation vibrations of the adsorbed molecules on AlSBA-15 samples.

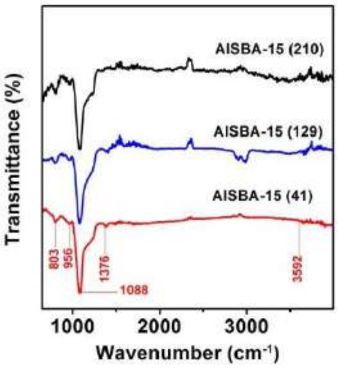


Figure 4. FT-IR spectra of AlSBA-15 catalysts with different *n*Si/*n*Al ratio.

TABLE 1. Elemental composition and textural properties of the AlSBA-15 materials.

S.No	n_{Si}/n_{Al} (gel)	n_{Si}/n_{Al} (product)	a_o (Å)	d_{100} (Å)	S_{BET} (m^2/g)	Dp (A°)	Vp (cm^3/g)	Total acidic sites (mmol/g)
1	7	41	116.4	100.8	480.2	54.5	0.654	0.42
2	14	129	108.9	94.3	563.4	53.5	0.759	0.20
3	28	210	101.8	91.3	757.4	48.9	0.93	0.11

S_{BET} = Specific surface area, Vp = Pore volume, Dp = Pore diameter, a_o = Unit cell constant was calculated as, $a_o = 2 \times d_{100}/\sqrt{3}$.

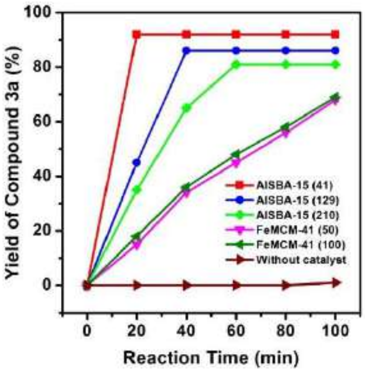


Figure 5. Time courses of α-aminonitrile 3a formation using various solid catalysts. Reaction conditions: compound 1a (3 mmol), compound 2a (3 mmol) and TMSCN (3 mmol) and catalyst (20 mg) in water medium at RT.

Catalytic activity

After the successful preparation and characterization of the AlSBA-15, we examined their catalytic activity in the Strecker reaction. In order to establish the optimal condition for Strecker reaction, we selected the model reaction between o-toluidine and 3-methoxybenzaldehyde in the presence of various heterogeneous catalysts at room temperature (RT) and at 50 °C. The catalytic activity of various heterogeneous catalysts used in the Strecker reaction is shown in Table 2. The model reactions were performed by varying the solvent and temperature with constant catalyst loading. As the temperature increases from RT to 50 °C (Table 2, Entries 1-6) increase in the product formation were observed in the solvents acetonitrile (ACN), toluene, ethanol, dichloromethane (DCM), 1,4-dioxane and N,N-dimethylformamide (DMF). But in the case of solvent free conditions, the reaction proceeds with moderate yield of 55 % and 85 % at RT and 50 °C respectively (Table 2, Entry 7). The reaction using AlSBA-15 (41) in water (Table 2, Entry 8) proceeded very well at RT and 50 °C in a short reaction time. AlSBA-15 (41) shows a high yield of compound 3a (96 %) within 20 min of reaction time than other two AlSBA-15 (129) and AlSBA-15 (210) catalysts. This is due to the low n_{Si}/n_{Al} ratio of AlSBA-15 (41) provides more acidity in comparison to AlSBA-15 (129) and AlSBA-15 (210), the later catalysts possess two and four times less acidity than AlSBA-15 (41) (Table 1). Hence, the formation of compound 3a takes a little long reaction time over AlSBA-15 (129) and AlSBA-15 (210) with the product yield of 94 % and 92 % in 45 min and 55 min, respectively. The Al content in the catalyst AlSBA-15 (129) & AlSBA-15 (210) is low accordingly which resulted a low product yield and required long reaction time. However the decrease in the product yield over AlSBA-15 (129) and (210) is not considerable in comparison with AlSBA-15 (45). The decrease in n_{Si}/n_{Al} ratio, that increases the acid strength of AlSBA-15 samples which is an important parameter in addition to density of acid sites of the catalyst.

The product yield of compound 3a was compared by carrying out the reactions with FeMCM-41 (50), FeMCM-41 (100) catalysts and without catalyst to study the efficiency of AlSBA-15 catalysts. The FeMCM-41 (50) and FeMCM-41(100) catalysts showed the compound 3a yield of 12 % and 8 % at RT and 68 % and 53 % at 50 °C, respectively (Table 2, Entry 11, 12). There was no product formation on the reaction performed without catalyst (Table 2, Entry 13). Therefore it is clearly indicates that the reaction is very well initiated and activated by the AlSBA-15 catalysts for high product yield of compound 3a in water medium. It is interesting to note that there is no formation of cyanohydrin (adduct between an aldehyde and trimethylsilyl cyanide) formation as it was observed the earlier reports [56], when the three components (amine, aldehyde and cyanide source) mixed together at once. In our methodology we mix three components together at once for the formation of α-aminonitriles and there were no by-product formation of cyanohydrin. This is due to the rapid formation of imine from amine on catalyst active sites and followed by the cyanide attack leads to the absolute quick formation of α-aminonitrile.

The one-pot catalytic synthesis of α-aminonitriles were carried out in water medium at room temperature using AlSBA-15 (41) catalyst with different catalyst amount viz., 5,10, 15, and 20 mg and the results were shown in Table 3**.** The yield of compound 3a increased from 75 to 96 % as increase in the catalyst amount from 5 to 15 mg. This is because increase in catalyst amount increases the number of active centre which can be used to catalyse the reaction and thus produces high yield of compound 3a. Further increase in the catalyst amount from 15 mg to 20 mg there were no increase in the product yield of compound 3a (96 %). This clearly indicates that the active sites present in the optimum AlSBA-15 (41) catalyst amount of 15 mg are high enough to produce the maximum product yield of compound 3a (96 %). A blank reaction was also carried out without the catalyst for 100 min and the compound of interest is not obtained (Table 3, Entry 5).

In the next study, we screened recovery of the catalyst for the Strecker reaction over six consecutive cycles. After the completion of the reaction (monitored through TLC), the catalyst was recovered from the reaction mixture by simple filtration, followed by EtOAc washing and then dried under vacuum at RT for 1 h. The recovered catalyst maintained high activity when reused for three times without any loss in its performance. This is much significance for the exploitation of the catalyst for different reactions. When we used the catalyst for 4-6 cycles the product formation is gradually decreased. The details were shown in Figure 6. This is due to some

TABLE 2. Screening of reaction conditions for the synthesis of compound 3a using various solid catalysts.

Entry	Catalyst	Time	Solvent	Temp. (°C)	Yield^a (%)
1	AlSBA-15 (41)	12 h	ACN	RT/50	30/71
2	AlSBA-15 (41)	12 h	Toluene	RT/50	15/45
3	AlSBA-15 (41)	12 h	Ethanol	RT/50	38/75
4	AlSBA-15 (41)	12 h	DCM	RT/50	25/85
5	AlSBA-15 (41)	12 h	Dioxane	RT/50	39/71
6	AlSBA-15 (41)	12 h	DMF	RT/50	62/84
7	AlSBA-15 (41)	6 h	Solvent free	RT/50	55/85
8	**AlSBA-15 (41)**	**20min**	**Water**	**RT/50**	**96/96**
9	AlSBA-5 (129)	45min	Water	RT/50	94/94
10	AlSBA-5 (210)	55min	Water	RT/50	92/92
11	FeMCM-41 (50)	2 h	Water	RT/50	12/68
12	FeMCM-41 (100)	2 h	Water	RT/50	08/53
13	Without catalyst	12 h	Water	RT/50	NP

Reaction conditions: amine 1a (3 mmol), aldehyde 2a (3 mmol), TMSCN (3 mmol) and catalyst (20 mg) under various solvent medium and temperature. A = Isolated yield. RT = Room temperature. NP = No product.

TABLE 3. Reactivity based on the amount of AlSBA-15 (41) for the one-pot synthesis of compound 3a.

Entry	Amount of AlSBA-15 (41)	Reaction time	Yield (%)^b
1	5 mg	20 min	75
2	10 mg	20 min	91
3	15 mg	20 min	96
4	20 mg	20 min	96
5	Without catalyst	100 min	NP

Reaction conditions: catalyst (5, 10, 15 & 20 mg), compound 1a (3 mmol), compound 2a, (3 mmol) and TMSCN (3 mmol) in water medium at RT. b = Isolated yield. NP = No product.

of the reactants or products would be strongly adsorbed on the AlSBA-15 (41) surface and blocks the active sites of the catalyst, which on subjected for the α-aminonitrile synthesis in the next cycle leading to the formation of product over longer times. The presence of the aluminium in AlSBA-15 catalyst causes a positive charge density, which can be considered as a strong Lewis acid site. On the other hand, the AlSBA-15 (41) catalyst gives a better performance when compared to AlSBA-15 (129) & AlSBA-15 (210) which is expected because of its strong acid number of sites are decreased accordingly, in accordance with the TPD-NH_3 analysis. We made the compounds 3a-3t by using this methodology; the resulted yields are range from 85-96 % and reaction completion time from 20-55 min.

The scope and the limitations of this novel reaction methodology were studied using various electron-donating and electron-withdrawing substituted amines as well as aryl/aliphatic aldehydes/ketones with TMSCN in the presence of AlSBA-15. Further this methodology was applied to various amine compounds containing electron-donating and electron-withdrawing groups at *ortho, meta & para* position to the 3-methoxy benzaldehyde. The results of this study showed a remarkable time difference and yield. Aromatic, hetero aromatic and aliphatic aldehydes were employed, however hetero cyclic aromatic aldehydes required a little long reaction time and aliphatic aldehydes required longer time when compared to the aromatic aldehydes due to the heterocyclic/aliphatic aldehyde resulted imine intermediate have low stability because of their retention time is low.

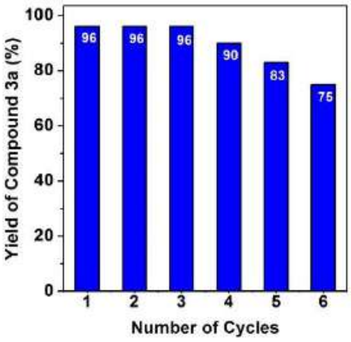
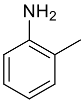
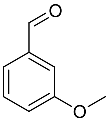
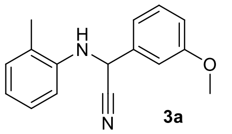
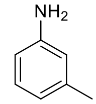
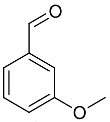
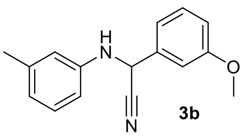
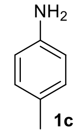
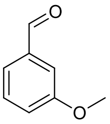
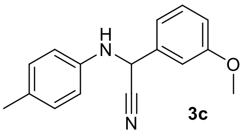
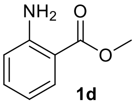
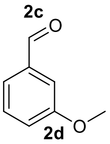
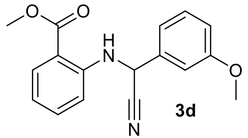
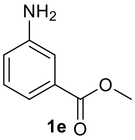
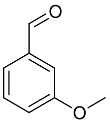
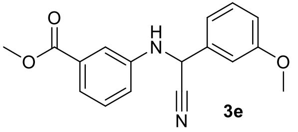
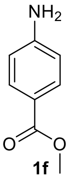
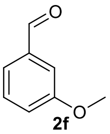
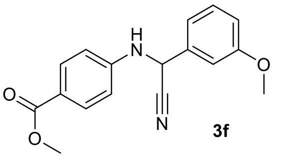
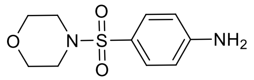
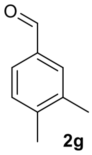
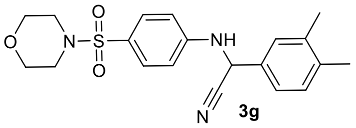
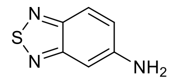
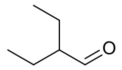
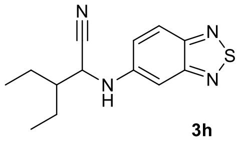
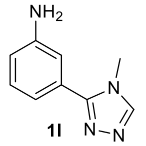
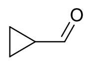
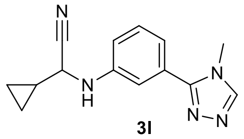
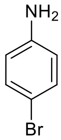
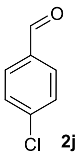
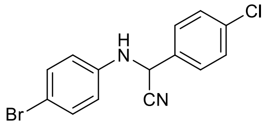
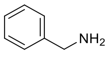
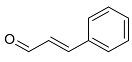
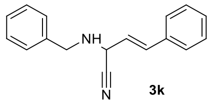
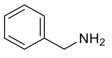
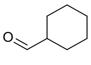
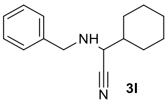
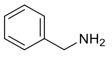
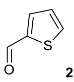
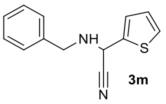
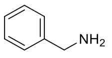
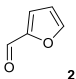
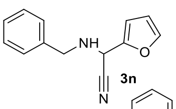
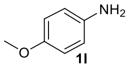
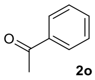
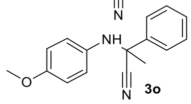
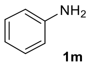
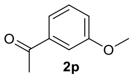
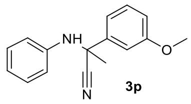
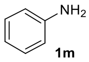
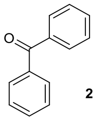
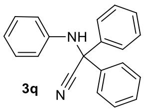
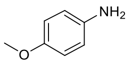
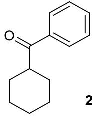
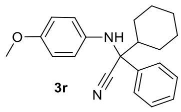
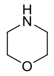
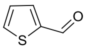
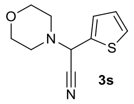
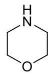
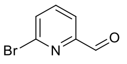
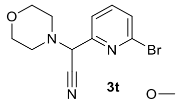
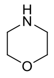
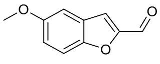
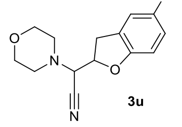


Figure 6. Recyclability of the catalyst. Reaction conditions: amine 1a (3 mmol), aldehyde 2a (3 mmol), TMSCN (3 mmol) and catalyst (15 mg) in water medium at RT for 20 min.

We studied the reaction between methyl (electron donating) group at *ortho, meta and para* substituted aniline and 3-methoxybenzaldehyde (Table 4, Entry 1-3) and the results of the *ortho* and *para* methyl substituted aniline showed a very high product yield 96 % and 95 %, respectively within 20 min of reaction time. Whereas the *meta* substituted methyl group at aniline showed a lower product yield of 91 % with a long reaction time of 35 min compare to *ortho* and *para* analogues. This is due to methyl group at *ortho* and *para* positions of aniline enrich the electron density on nitrogen of aniline and it favors the nucleophilic attack on the carbonyl group of aldehyde. In case of CH_3COOCH_3, electron withdrawing group substituted at *ortho, meta and para* position of aniline, the *meta* substituted aniline showed a high product yield of 95 % within 35 min, whereas *ortho* and *para* isomers showed a longer reaction time of 50 min and 55 min with the product yield of 94 % and 93 %, respectively (Table 4, Entry 4-6). This is due to the electron withdrawing group at the *ortho* and *para* position of aniline deactivates the amine group and decreases the electron density on nitrogen atom and it decreases the rate of attack of amine to the carbonyl group of aldehyde. This kind of deactivation of amine group is less in the case of CH_3COOCH_3, electron withdrawing group at the *meta* position towards amine group than the *ortho* and *para* isomers. Hence, electron withdrawing group at *meta* position of aniline is more active for the nucleophilic attack than *ortho* and *para* substituted aniline. We also carried out the reaction between different amines and aldehydes/ketones and found that the reaction with benzyl amine had very short

TABLE 4. α-Aminonitrile synthesis from various amine compounds.

Entry	Amine compound	Aldehyde/Ketone	Product	Time (min.)	Yield[a] (%)
1	 **1a**	 **2a**	 **3a**	20	96
2	 **1b**	 **2b**	 **3b**	35	91
3	 **1c**	 **2c**	 **3c**	20	95
4	 **1d**	 **2d**	 **3d**	50	94
5	 **1e**	 **2e**	 **3e**	35	95
6	 **1f**	 **2f**	 **3f**	55	93
7	 **1g**	 **2g**	 **3g**	50	94
8	 **1h**	 **2h**	 **3h**	55	81
9	 **1l**	 **2l**	 **3l**	49	82
10	 **1j**	 **2j**	 **3j**	28	91

11	 **1k**	 **2k**	 **3k**	20	94[57,b]
12	 **1k**	 **2l**	 **3l**	20	95[58,b]
13	 **1k**	 **2m**	 **3m**	20	95[59,b]
14	 **1k**	 **2n**	 **3n**	20	94[60,b]
15	 **1l**	 **2o**	 **3o**	25	91[60,b]
16	 **1m**	 **2p**	 **3p**	25	91[61,b]
17	 **1m**	 **2q**	 **3q**	25	93[62,b]
18	 **1l**	 **2r**	 **3r**	25	92[60,b]
19	 **1n**	 **2m**	 **3s**	55	85[63,b]
20	 **1n**	 **2s**	 **3t**	55	87[63,b]
21	 **1n**	 **2t**	 **3u**	50	85[63,b]

Reaction conditions: amine compound (3 mmol), aldehyde/keto compound (3 mmol), TMSCN (3 mmol) and AlSBA-15 (41) (15 mg) in water (5 ml) were stirred at RT for the appropriate amount of time (20-55 min). a = Isolated yield. b = The spectral data (^{1}H, ^{13}C NMR) of known compounds were found to be identical with those reported in the literature.

reaction time and high yield (Table 4, Entries 13-16). We carried out the reaction with keto compounds, the reaction preceded very well with high yield (Table 4, Entries 17-18). When we carried out the reaction using secondary amines, the reaction was preceded moderately and taken little longer time (Table 4, Entries 21-23).

We studied the possibility of this method to be a convenient scale-up process for the preparation α-aminonitriles (Table 4, Entry 1) on 10 g scale and 25 g scale and the results showed a 96 % and 95 % of product yield, respectively. There is no remarkable yield difference between R&D scale (Table 4, Entry 1) and scale up process. This study clearly indicates that this methodology is convenient for a scale-up process.

To clarify the catalytic role, reaction pathway and rate of reaction in one-pot synthesis, we analysed the crude samples obtained at various time intervals of 10, and 20 min using ^{1}H NMR ($CDCl_3$, 400 MHz) and the spectra are shown in Figure 7. The ^{1}H NMR spectrum (a) showed that our catalyst promoted the conversion of amine, aldehyde to imine compound and corresponding peaks due to amine, aldehyde, imine and TMSCN were marked. The ^{1}H NMR spectrum is showing the complete conversion and formation of compound 3a after 20 min. This study also proves that the reaction path way proceeds via imine formation first and followed by cyanide attack, for the compound 3a formation.

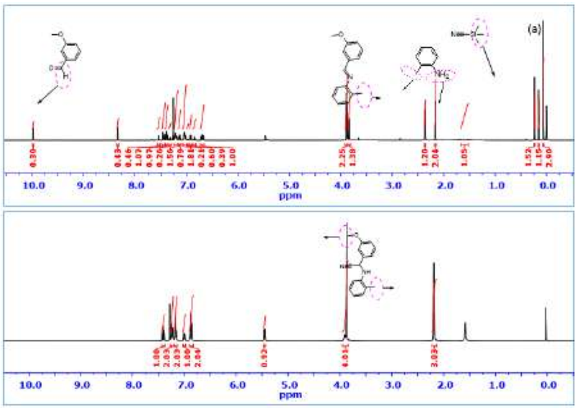


Figure 7. ^{1}H NMR tracing experiment for the synthesis of compound 3a at various time intervals of (a) 10 min and (b) 20 min. Reaction condition: amine 1a (3 mmol), aldehyde 2a (3 mmol), TMSCN (3 mmol) and catalyst (15 mg) in water medium at RT for 20 min.

To understand the decrease in catalytic efficiency, we carried out the NH_3-TPD experiment for fresh and reused AlSBA-15 (41) after six reaction cycle to determine acid sites concentration (Figure 8). To do this, after the completion of reaction, the reaction mixture was dissolved in ethyl acetate (2 ml), followed by filtration through Whatman filter paper and the solid was washed twice by the ethyl acetate (1 ml) to avoid the loss of product yield. The organic layer contains the desired product. The recovered catalyst was dried at 100 °C in order to remove the volatiles and reused the same catalyst in a subsequent reaction. Smooth loss of catalyst activity was observed from fourth reaction run due to the decrease in the concentration of acid sites on the catalyst surface as shown in Figure 8. The NH_3-TPD profile of the fresh AlSBA-15 (41) catalyst showed of three peaks at *ca.* 216, 483 and 734 °C due to weak, medium, and strong acid sites, respectively. The reused AlSBA-15 (41) catalyst showed only two peaks at around 242 and 496 °C due to weak and medium acid sites, respectively with complete disappearance of strong acid sites at around 734 °C. The considerable decrease in peak intensity was observed in the reused catalyst than the fresh catalyst. The decrease in peak intensity and the disappearance of strong acid sites is due to the strong adsorption of reactants or product or intermediate on the acid sites and decreases acid sites concentration on AlSBA-15 (41) surface. The decrease in acid site concentration of AlSBA-15 (41) is the major cause for the drop in product yield.

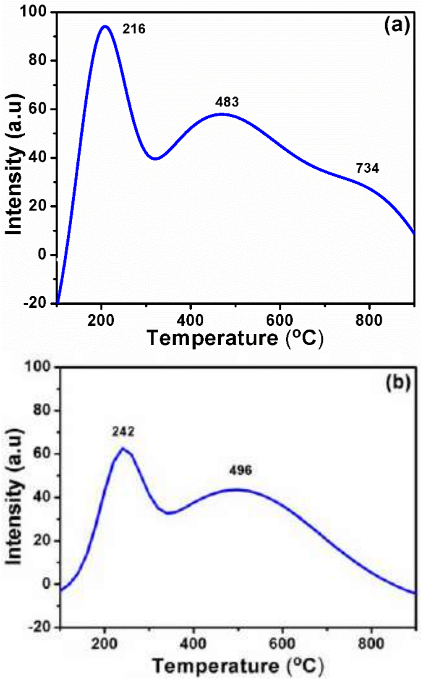


Figure 8. NH_3-TPD profile of AlSBA-15 (41): (a) fresh catalyst and (b) reused after six reaction run.

From the above results, to the best of our knowledge, plausible mechanism is proposed for the process of Strecker reaction using AlSBA-15 (Figure 9). The imine synthesis (intermediate II) is the slow step for Strecker reaction. Therefore, we may surmise that the AlSBA-15 catalyst resulted in an improvement in the reaction rate for the synthesis of this intermediate. At first, the aldehyde will interact with Lewis acid sites of AlSBA-15 which resulted complex (I). In the second step, the aniline will attack complex (I) resulted the corresponding imine

(II) by removal of H_2O. After this step, imine (II) will undergo an attack by cyanide anion from TMSCN, which resulted to produce compound 3a.

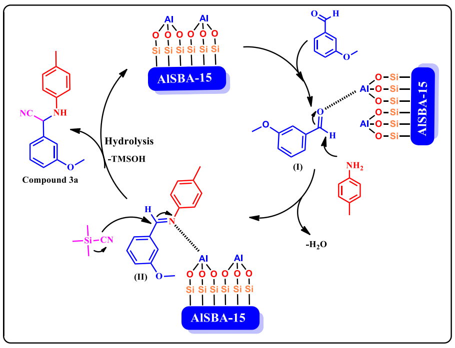


Figure 9. Plausible mechanism pathway for the one-pot synthesis of α-aminonitriles using AlSBA-15 catalyst.

CONCLUSION

In this work we report for the first time a rapid and highly efficient protocol for one-pot synthesis of α-aminonitriles *via* reduction by Strecker reaction. The one-pot, three component system using amine (primary/secondary), carbonyl compounds (aldehydes/ketones) and TMSCN proceeds well in presence of AlSBA-15 with an excellent product yield (85-96 %). We have described herein the AlSBA-15 as an efficient, eco-friendly catalyst for various α-aminonitriles synthesis in one-pot. We found this methodology is convenient for the scale-up process and tolerates a variety of functional groups, various electron-donating and with-drawing groups with wide substrate scope. The advantages of this method are: (1) The reaction carried out in water, (2) Reusability of the catalyst up to 6 cycles, (3) High chemo selectivity, (4) Short reaction time, (5) Excellent yields, (6) Easy isolation/ purification, (7) The use of relatively non-toxic reagents (operationally simple) in the reaction media and (8) Two-step synthesis reduced to one-pot under greener approach.

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Persian Abstract

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چکیده

کاتالیزور آلومینواسلیکا نوع AlSBA-15 (x) نانومقیاس نانو با نسبت nSi / nAl متفاوت (x = 41، 129 و ۲۱۰) با استفاده از روش هیدروترمال سنتز شد. کاتالیزور AlSBA-15 با استفاده از XRD، جذب N2، TPD-NH3، FT-IR، SEM و TEM مشخص شد. تجزیه و تحلیل XRD از کاتالیست های AlSBA-15، حضور ساختار کریستالی مرتب با تقارن p6mm را تایید کرد. ایزوترم N2 مواد کاتالیزور AlSBA-15 نشان دهنده یک ایزوترم جذب نوع IV با حلقه هیستریزی H1 بود. سطح مخصوص و حجم منفذ خاص کاتالیزور AlSBA-15 در معرض خشم ۴۸۰ تا ۷۵۷ مترمکعول در گرم و از ۰٫۶۵ تا ۰٫۹۵ سانتی متر بر گرم است. تجزیه و تحلیل SEM AlSBA-15 (۴۱) نشان داد که مورفولوژی ذرات کرم مانند ذرات در محدوده اندازه ۳ میکرومتر با وجود وجود ذرات کوچکتر حدود اندازه ی ۱ میکرومتر. یک رویکرد متمایز برای سنتز α-آمینونیتیل ها با استفاده از کاتالیزور نانوذرات AlSBA-15 ناهمگن از طریق واکنش استریک. این سیستم یکپارچه، سیستم سه

جزء آمین (اولیه / ثانویه)، ترکیبات کربنیل (آلدئیدها / کتون) و ترکیبات TMSCN در حضور کاتالیزور AlSBA-15 در محیط آب در دمای اتاق (RT) عالی عمل می کند. مزایای عمده عبارتند از عملکرد عالی، زمان واکنش کوتاه، انتخاب شیمیایی بالا، روش تجربی ساده، بازیافت کاتالیزور، روش کار آسان. این سنتز یک گلدان شامل دو مرحله متوالی است: (۱) تشکیل ایزوم از آمین و آلدئید / کتون و (۲) افزودن سایانو به امین. یافته ها نشان می دهد که کاتالیزور قابل بازیافت است و می تواند تا شش دوره مجددا استفاده شود.