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Nanosilica chloride catalyzed one-pot three-component synthesis of 1,4- dihydropyridines via the Hantzsch reaction at ambient temperature

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Abstract

Nanosilica chloride has been employed as an efficient, heterogeneous and effective catalyst in the preparation of 1,4- dihydropyridines (1,4-DHPs) under mild reaction conditions. Simple workup procedure, short reaction time, reusability of the catalyst and good to excellent yield of the product, are other advantages of this catalyst.

Keywords: Nanosilica chloride, Three-component reactions, Hantzsch reaction, dihydropyridines, Heterogeneous catalyst

1. Introduction

Hantzsch 1,4-dihydropyridines (1,4-DHPs) are well known as Ca^{2+} channel blockers, and have emerged as one of the most important classes of drugs for the treatment of cardiovascular diseases, including hypertension [1]. The DHP heterocyclic ring is a common feature of various bioactive compounds such as vasodilator, bronchodilator, antiatherosclerotic, antitumor, geroprotective, hepatoprotective and antidiabetic agents [2]. Recent studies have revealed that 1,4-DHPs exhibit several other medicinal applications which include neuroprotectant and platelet anti-aggregratory activity, in addition to acting as a cerebral antiischemic agent in the treatment of Alzheimer's disease and as a chemosensitizer in tumor therapy [3]. These examples clearly demonstrate the remarkable potential of novel DHP derivatives as a source of valuable drug candidates.

In recent years, much attention has been focused on the synthesis of 1,4-dihydropyridyl compounds, due to their significant biological activity. For these

reasons, polyhydroquinoline compounds not only have attracted the attention of chemists to synthesize but also represent an interesting research challenge. Numerous methods have been reported for the synthesis of polyhydroquinoline derivatives, because of the biological importance associated with these compounds. The classical method involves the three-component coupling of an aldehyde with ethyl acetoacetate, and ammonia in acetic acid or in refluxing alcohol [5,6]. However, these methods suffer from several drawbacks such as a long reaction time, an excess of organic solvent, lower product yields, and harsh refluxing conditions. Thus, chemists have developed several alternate and more efficient methods for the synthesis of polyhydroquinoline derivatives, which include the use of microwaves [7], ionic liquids [8], refluxing at high temperature [9], TMSCl–NaI [10], metal triflates [11], and I_2 [12]. However, the use of high temperatures, expensive metal precursors, catalyst that are harmful to the environment, and long reaction times limits the use of these methods. Thus, the development of a simple and efficient method for the preparation of 1,4-dihydropyridines derivatives is an active area of research and there is scope for further improvement involving milder reaction conditions and higher product yields. Therefore, the search for a better catalyst for the synthesis of dihydropyridines derivatives using less hazardous solvents or solvent free conditions is of prime importance.

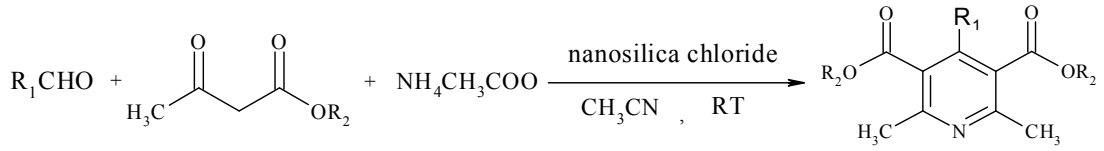
Recently, there has been an increasing interest in developing greener processes [13]. In this context, heterogeneous catalysis [14] is emerging as an alternative to homogeneous processes since catalyst can be recovered after the reaction and re-used several times to achieve very high turn-over numbers. Silica gel is one of the extensively used surface material supports for different chemical transformations in organic chemistry [15]. One such modified silica is silica chloride (SiO_2-Cl), which was easily prepared from silica gel and thionyl chloride, is a good solid catalyst [16-20] in term of convenience, easy production, insolubility in all organic solvent and has been reported to be an efficient reagent in the synthesis of organic compounds. [21]

We have already reported the use of silica chloride as analogue of trimethylsilyl chloride, for the efficient conversion of sulfoxides into sulfides [22], deprotection of organic compounds [23] and reductive amination of aldehydes and ketones [24]. It has been used also in different organic transformations [25-27]

We modified nano silica gel surface by using ultrasonic and thionyl chloride, which acts as a mild and efficient catalyst, and can be a useful and cheap catalyst for the synthesis of 1,4-dihydropyridines. Our studies have shown that thionyl chloride is a satisfactory chlorinating agent for nanosilica and amorphous silica, if used with sonication. This method gives values for active silanols per unit area of silica surface, comparable to other method, for determining available activities. Nano silica chloride was prepared by the readily available material and can also be easily removed from the reaction mixture.

As a part of our on-going research program directed towards the development of new and rapid synthetic methods for the construction of biologically active structural motifs, we intended to develop a rapid, efficient, economic and easy to scale-up method for Hantzsch reaction. Our aim in undertaking this work was to overcome the

limitations and draw backs of reported methods. Here in, we report a rapid, efficient , economic , environmentally benign and easy to scale-up method for the synthesis of 1,4-dihydropyridines using silica chloride as a heterogeneous catalyst at room temperature. (Scheme 1)



Scheme1: Synthesis of 1,4-dihydropyridines catalyzed by nanosilica chloride

2.Experimental

2.1.Materais and general procedures

Nanosilica gel with average grain size(10 nm) and specific surface area(>600 m^2/g) was purchased from US Research Nanomaterial and other materials purchased from Alderich and Merk chemical company. All melting point were determined on a Perfit melting point apparatus and are uncorrected . HNMR spectra were registered on a PPx- 300 NMR spectrometer (300MHz) in $CDCl_3$+DMSo-d_6/DMSo-d_6 using tetramethyle silan as an internal standard and IR spectra were recorded on (Perkin Elmer FTIR) spectrometer using KBr discs. Mass spectrum data was recorded on Joll jms d-300 mass spectrometer at 70 ev. sonycation was carried out with Hielscher UP2005.

2.2. Preparation of Nanosilica chloride

Into a 200 ml beaker, 5.0 g silica nanoparticles oven-dried (120 ℃) and 100 ml dichloro methane were mixed and dispersed with ultrasonic vibration for two times, each time lasted for 30 min. Then, the mixture was poured in to round bottomed flask (250 ml) equipped with a condenser and a drying tube, was added thionyl chloride (toxic and should be used with caution) (30 ml) and refluxed for 72 hours. The excess thionyl chloride and solvent was removed to dryness under reduced pressure. The nanosilica chloride was dried in vacuo at 90 ^oC and the resulting greyish powder was stored in a desicator under vacuum. The chlorosilyl groups on silica surface (2.2 mmol) was determined by suspension of reagent (0.1 g) in $NaHCO_3$ solution (0.05 M, 10 ml) and titrating with silver nitrate solution (0. 1 M, 22 ml) using potassium chromate as indicator.

2.3. General procedure for the Hantzsch reaction.

To mixture of aldehyde (1 mmol) , 1,3 dicarbonyl compound (2 mmol), ammonium acetate (2 mmol) in CH_3CN(5 ml), nanosilica chloride (0.02 g) was added and stirring was continued at room temperature for 30-45 min. After completion of the reaction (monitored by TLC), the catalyst was removed by filteration and solvent evaporated in reduced pressure. The resulting solid product was recrystalized from ethanol to give pure 1,4-DHPs. Products were identified by comparison with authentic

samples and by ^{1}H and ^{13}C NMR and their melting points. Spectroscopic data for selected products are shown below.

Compound of entry 1: Mp = 156–158 8C. ^{1}HNMR: d = 1.25 (t, J = 7.1 Hz, 6 H), 2.32 (s, 3 H), 2.33 (s, 3 H), 4.11 (q, J = 7.1 Hz, 4 H), 5.01 (s, 1 H), 5.97 (br s, 1 H, NH), 7.11–7.32 (m, 5 H). ^{13}C NMR: d = 14.1, 19.5, 39.4, 59.3, 104.1, 127.5, 128.8, 135.7, 144.1, 145.9, 167.8. IR (KBr): 3334, 1690, 1654, 1494, 1243, 1127, 721 cm^{-1}. Compound of entry 2: Mp = 144–146 8C. ^{1}H NMR: d = 1.24 (t, J = 7.2 Hz, 6 H), 2.33 (s, 6 H), 4.11 (q, J = 7.2 Hz, 4 H), 4.97 (s, 1 H), 5.88 (br s, 1 H, NH), 7.23–7.19 (m, 4 H). 13C NMR: d = 14.3, 19.6, 39.2, 59.9, 103.8, 127.9, 129.4, 131.7, 144.1, 146.3, 167.5. IR (KBr): 3360, 1695, 1651, 1487, 1212, 1122, 789 cm^{-1}. Compound of entry 3: Mp = 130–132 8C. ^{1}H NMR: d = 1.23 (t, J = 7.1 Hz, 6 H), 2.35 (s, 6 H), 4.13 (q, J = 7.1 Hz, 4 H), 5.10 (s, 1 H), 6.16 (br s, 1 H, NH), 7.50 (d, J = 8.6 Hz, 2 H), 8.14 (d, J = 8.6 Hz, 2 H). ^{13}C NMR: d = 14.2, 19.5, 40.1, 60.3, 103.0, 123.6, 128.9, 145.0, 146.2, 155.2, 167.2. IR (KBr): 3317, 1705, 1647, 1521, 1348, 1215, 1122, 707 cm^{-1}. Compound of entry 4: Mp = 160–162 8C. ^{1}H NMR: d = 1.24 (t, J = 7.1 Hz, 6 H), 2.34 (s, 6 H), 4.12 (q, J = 7.1 Hz, 4 H), 5.32 (s, 1 H), 5.77 (br s, 1 H, NH), 7.18 (d, J = 8.4 Hz, 2 H), 7.34 (d, J = 8.4 Hz, 2 H). ^{13}C NMR: d = 4.1, 19.3, 39.4, 59.8, 103.9, 127.9, 130.9, 130.4, 142.3, 148.5, 167.8. IR (KBr): 3340, 1690, 1643, 1492, 1211, 1120, 770 cm^{-1}. Compound of entry 5: Mp = 230–232 8C. ^{1}H NMR: d = 1.25 (t, J = 7.1 Hz, 6 H), 2.34 (s, 6 H), 4.12 (q, J = 7.1 Hz, 4 H), 5.32 (s, 1 H), 5.77 (br s, 1 H, NH), 6.65 (d, J = 8.9 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H). ^{13}C NMR: d = 14.1, 19.3, 39.4, 59.8, 103.9, 127.9, 130.9, 130.4, 142.3, 148.5, 167.8. IR (KBr): 3331, 1689, 1656, 1490, 1244, 1126, 720 cm^{-1}. Compound of entry 6: Mp = 135–137 8C. ^{1}H NMR: d = 1.28 (t, J = 7.1 Hz, 6 H), 2.30 (s, 3 H), 2.32 (s, 6 H), 4.14 (q, J = 7.1 Hz, 4 H), 4.98 (s, 1 H), 6.09 (br s, 1 H, NH), 7.04 (d, J = 7.8 Hz, 2 H), 7.23 (d, J = 7.8 Hz, 2 H). ^{13}C NMR: d = 14.3, 19.4, 21.2, 39.1, 59.7, 103.9, 127.8, 128.9, 135.2, 144.3, 145.0, 168.0. IR (KBr): 3343, 1690, 1651, 1491, 1213, 1122, 772 cm^{-1}. Compound of entry 7: Solid; Mp = 117–121 8C. ^{1}H NMR: d = 2.35 (s, 6 H), 3.72 (s, 6 H), 4.55 (d, J = 7.24 Hz, 1 H), 5.62 (br s, 1 H, NH), 6.17–6.19 (m, 2 H), 7.10–7.40 (m, 5 H). ^{13}CNMR: d = 14.2, 19.3, 36.2, 51.1, 102.2, 126.3, 126.9, 128.0, 128.3, 131.8, 137.7, 145.4, 168.1. IR (KBr): 3335, 2949, 1700, 1650 cm^{-1}.

3. Results and discussion

At the beginning to study the effect of catalyst and catalyst loading on the yield of the Hantzsch reaction, the reaction of benzaldehyde and ethyleacetoacetate with ammonium acetate was chosen as a model reaction (Table 2, entry 1). To illustrate the need of nanosilica chloride for this condensation we examined the model reaction in the absence and in the presence of different amounts of the catalyst. The result shown in the Table 1. In the absence of the catalyst the reaction in refluxing ethanol After 18 hours, only 46% of product was obtained after recrystallization of the crude product from ethanol (entry 1, Table 1).

This results obviously shows the important role of the nanosilica chloride in this condensation. When benzaldehyde (1 mmol), ethyleacetoacetate (2 mmol) and

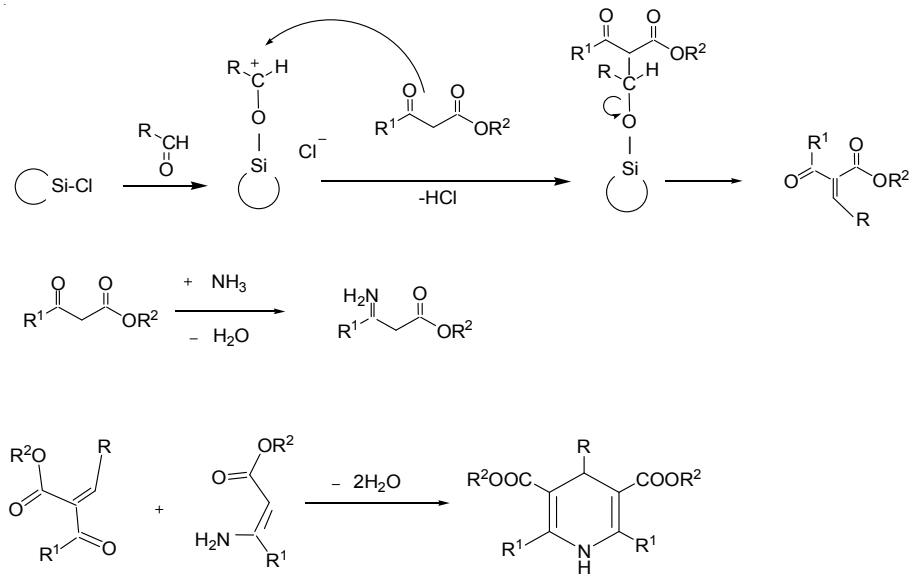
ammonium acetate (2 mmol) were stirred with different amounts of the catalyst, a loading of 0.02 gr silica chloride gave high yield of corresponding 1,4 DHP after 30 minutes (Table 1, entry 4). Lower and higher loading of the catalyst reduced the yield of the reaction (Table 1, entries 2,3 and 5,6).

Table 1. Condensationl of benzaldehyde, ethyl acetoacetate and ammonium acetate in the presence of different amounts of Nanosilica chloride.

[a]Entry	Catalyst loading (g)	t (min)	Yield (%)
[b]1	No catalyst	18 (h)	46
2	0.010	30	79
3	0.015	30	82
4	0.020	30	89
5	0.025	30	83
6	0.030	30	78

[a] Reaction conditions; benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol), ammonium acetate (2) mmol at room temperature. [b] in reflux condition

Mechanistically, it is assumed that nanosilica chloride can accelerate the reaction by forming oxygen-silicon bond, as described in the literature, [15-18] The mode of action of catalyst is illustrated in Scheme 2. The Si-Cl bond is labile and can give rise to Lewis acid centers on silica. The Cl is easily displaced selectively by the oxygen atom of aldehyde by the nucleophilic substitution reaction generating a cationic center on the carbonyl carbon which is easily attacked by the nucleophile, i.e. amonia to form the iminium ion. Interception of the iminium ion by the 1,3 dicarbonyl compound cyclizes to dihydropyrimidinone.



Scheme 2: Suggested mechanism

In order to examine scope of the method, a variety of aromatic aldehydes with different substituent groups condensed with alkyl acetoacetate esters and ammonium acetate under optimal reaction conditions and a good to excellent yields of the corresponding 1,4 DHPs were obtained (Table 2). As it is clear from table 2, both electron withdrawing and electron releasing groups on the aromatic ring of the aldehydes gave high yield of the corresponding 1,4-dihydropyridines. (Table 2, entries 2-6 and entries 7-9). It is interesting to mention that acid-sensitive group such as carbon-carbon double bonds and thio-group were not affected under the reaction conditions and high yield of the corresponding 1,4 DHPs obtained (Table 2, entries 10, 12). The study was extended to aliphatic (entries 14 - 16) aldehydes furnishing the products by a smooth cyclocondensation within 45 min. The yields in general are high regardless of the structural variations in aldehyde. The results are summarized in Table 2.

Table 2. Naosilica chloride catalyzed synthesis of 1,4-dihydropyridines[a]

Entry	R_1	R_2	Time (min)	Yield (%)[b]
1	Ph	Et	30	89
2	4-Cl-ph	Et	45	92
3	4-NO_2-ph	Et	30	91
4	2-NO_2-ph	Et	30	88
5	3-Br-ph	Et	45	89
6	4-Br-ph	Et	45	87
7	4-HO-C_6H_4	Et	30	91
8	4-Me-ph	Et	45	87
9	4-MeO-ph	Et	30	92
10	ph-C=C	Me	45	89
11	α-Naphtyle	Et	45	85
12	thien-2-yl	Et	45	89
13	fur-2-yl	Et	30	92
14	cyclohexyle	Et	45	86
15	n-pentyle	Et	45	88
16	Iso-Pr	Et	45	86

[a] Reaction condition: aldehyde (1 mmol), acetoacetate ester (2 mmol), NH_4OAc (2 mmol),
CH_3CN(5 ml) catalyst 0.02 g at room temperature.
[b] Isolated yield

In order to study the solvent effect over the reaction and comparison of efficiency of catalysts, we carried out the reactions in different solvents. We found that with non polar solvents like CH_2Cl_2 and THF, poor yields were obtained. In more polar solvents like methanol and ethanol better yields were obtained. However, the best result was obtained with CH_3CN (Table 3).

Table 3. Comparative study of solvent effect over catalyzed reaction.

Entry	Solvent	t(h)	Yield (%)
1	CH_2Cl_2	0.5	37
2	THF	0.5	31
3	CH_3CN	0.5	89
4	MeOH	0.5	48
5	EtOH	0.5	55

Reaction conditions; benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol), ammonium acetate (2) mmol, catalyst 0.02 g at room temperature.

Next, the reusability of the catalyst was studied. In this regard, a series of four consecutive runs of the model reaction were carried out and the results are tabulated in Table 4.

Table 4. Reusaability of NanoSilica chloride in one-pot synthesis of 3,4-Dihidropyrimidinones

Run	Chloride contents (meq/g)	Reaction time (min)	%yield[a]
1	2.1	30	89
2	1.6	30	81
3	1.3	30	75
4	0.9	30	65
[b]5	1.9	30	87

[a] Result refer to entry 1 in Table 2

[b] Refer to reactivated Nanoslilica chloride with thionyl chloride.

As it is clear from the table 4, there is a progressive decrease in isolated yield as well as chloride content of recovered catalyst decreased. (Table 4 entries 1-4). This may be due to lose of HCl during every run. However when the recovered catalyst was reactivated with thionyl chloride and reused as catalyst in the model reaction, the expected yield was obtained (Table 4 entry 5).

In order to explode the advantages and drawbacks of this method, the model reaction was compared with some of the reported results in the literature in Table 5.

Table 5. Comparison of Hantzsch reaction using different catalyst

Entry	Catalyst	T (^{o}C)	t (h)	Yield (%)	Ref.
1	-	100	18	46	[30]
2	$FeCl_3{\cdot}6H_2O$	100	4	49	[29]
3	CuCl	100	4	54	[29]
4	$ZnCl_2$	78	4	57	[29]
5	$InCl_3$	100	4	60	[29]
6	$PhB(OH)_2$	80	4	90	[30]
7	NanoSilica chloride	RT	0.5	86	This work

In order to determine the efficiency of nanosilica chloride as catalyst, the same reactions were carried out with other commercially catalysts ($FeCl_3{\cdot}6H_2O$, CuCl, $ZnCl_2$, $InCl_3$ and $PhB(OH)_2$) employed in related condensations [29,30]. The results summarized in Table 4 revealed that these systems gave lower yields of the desired product, even with high catalyst loadings. Furthermore, several side products could be observed (entries 2–5). The data in Table 5, clearly demonstrates the preference of nanosilica chloride as a heterogeneous catalyst in the Hantzch reaction in compare on with other catalysts in term of the reaction time. With respect to reaction times, yields of obtained products. It is clear from the results show in Table 5, which Hantzch reaction carried out with nanosilica chloride require shorter reaction time, lower temperature and higher yield.

To study the surface topography and to assess the surface dispersion of the active components over the SiO_2 substrate, SEM investigation was performed on a sample. The obtained representative electron micrographs are presented in Fig. 1(a,b) respectively. Since backscattered electrons (BSE) consist of high-energy electrons originating in the electron beam, that are reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with specimen atoms, thus heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and appear brighter in the image. On the other hand, BSE are used to detect contrast between areas with different chemical compositions [28]. It is believed that the bright spots in hybrids of system is heavier. Thus, it can be seen from Fig. 1(a,b) that some heavier chlorine atoms replacement of some lighter OH group on silicagel surface. The analysis of the back scattering SEM (BSE) of catalyst and calculation of particles size based on Clemex software, indicates the nanosilica chloride with a minimum size distribution 9-45 nm.

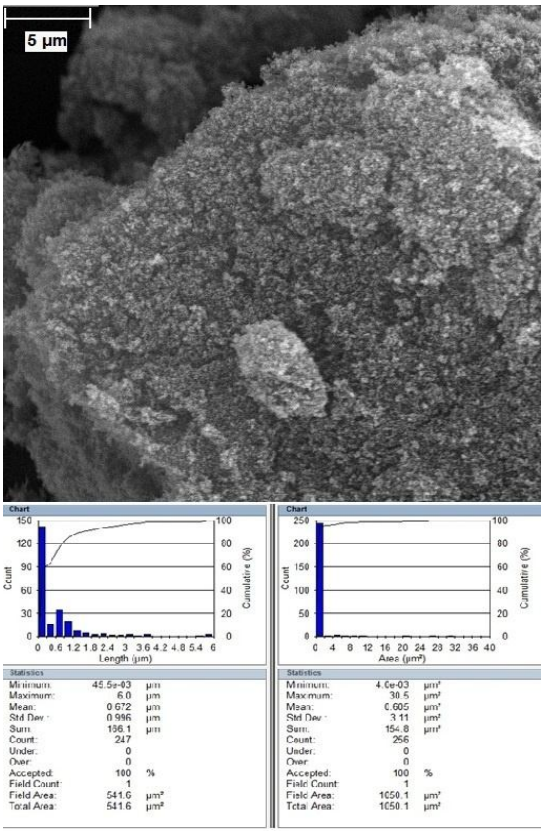


Fig. 1a: BSE of Nano silica

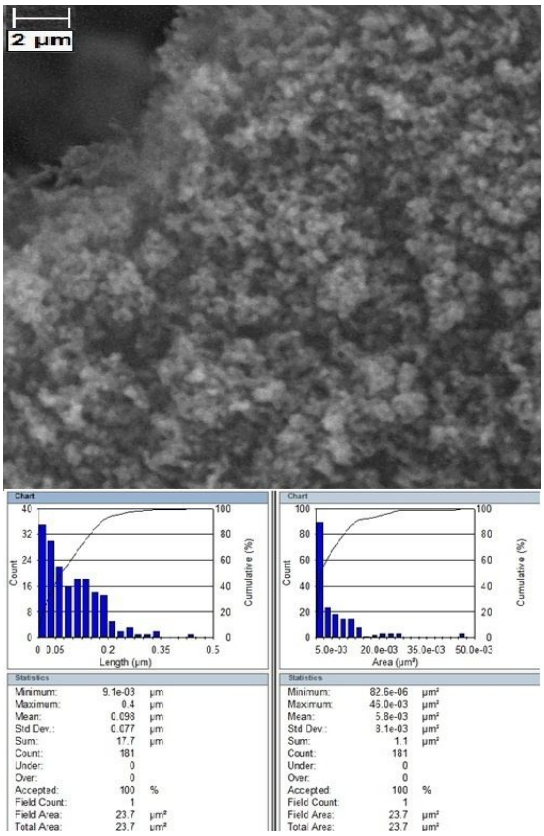


Fig. 1b: BSE of Nano silica

4. Conclusion:

In conclusion, we have shown that nanosilica chloride can catalyze efficiently the synthesis of 1,4-dihydropyridines by a one-pot three component condensation of aromatic aldehydes, alkyle acetoacetates and ammonium acetate. The main advantage of this method is that it requires short reaction times and carried out solvent free with simple work up and with excellent yields. Another advantage of this method is the selectivity between aromatic and aliphatic aldehydes. We believe that the nanosilica chloride is a convenient, attractive, reusable catalyst and bengin for synthesis of 1,4-dihydropyridines.

Acknowledgment

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