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Expanded Perlite-Polyphosphoric Acid (EP-PPA) as a Low-Cost Heterogeneous Solid Acid Catalyst for Green and Metal-Free Synthesis of Nitriles from Aldehydes

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Abstract: Expanded Perlite-Polyphosphoric Acid (EP-PPA) as a solid acid catalyst reported earlier by our group, has been found to be very effective for direct transformation of aldehydes into nitriles. The aforesaid catalyst exhibited excellent catalytic activity in high yielding preparation of a wide range of nitriles under solvent-free conditions. Furthermore, the method consistently has the advantages of environmental acceptability, short reaction times, excellent functional group compatibility and easy experimental and work-up procedures. Importantly, catalyst reusability up to six runs with little loss of catalytic activity made the present procedure better than the most previously reported protocols.

Keywords: Expanded Perlite-Polyphosphoric Acid (EP-PPA), heterogeneous catalyst, reusable catalyst, nitrile, aldehyde, solvent free.

INTRODUCTION

In synthetic organic chemistry, functional groups (particularly nitrile group) play a vital role. Due to easy transformation of nitriles into different functional groups, nitrile derivatives have been highlighted for the synthesis of many magnificent functional compounds such as esters, amides, amines, aldehydes, carboxylic acids, and heterocycles.[1–4] Furthermore, various nitrile-containing compounds are versatile building blocks in the synthesis of natural products, pharmaceuticals, agricultural chemicals and dyes.[5–10] Consequently, the significant synthetic properties of nitrile (as an important and productive functional) group have ensured long-standing studies of their utilization in research and industrial chemistry. The nucleophilic displacement of halogen compounds, aryl sulfonates, alcohols, esters, ethers, nitro or amino compounds and diazonium salts with inorganic cyanide ions is the most common and well-known classical method for the nitrile synthesis.[11–18] In addition, dehydration of amides[19–23] and aldoximes,[24–35] conversion of alcohols,[36–41] aldehydes,[42–64] carboxylic acids,[65–70] and amines[71–79] to nitriles using various reagents are the other alternative procedures. Because of the ready availability of aldehydes, direct conversion of aldehydes into nitriles with different compounds as nitrogen sources (without isolation of nitrogen-containing intermediates) have been utilized as an attractive method.[48,80–90] By considering some serious drawbacks of this method, a desired solution to synthesize nitriles from aldehydes (as a more serviceable and mild way) does need to be underway for organic chemistry. By now, plentiful reports can be found in the literature demonstrating the enormous changes in this methodology by synthetic chemists.[83,91,92]

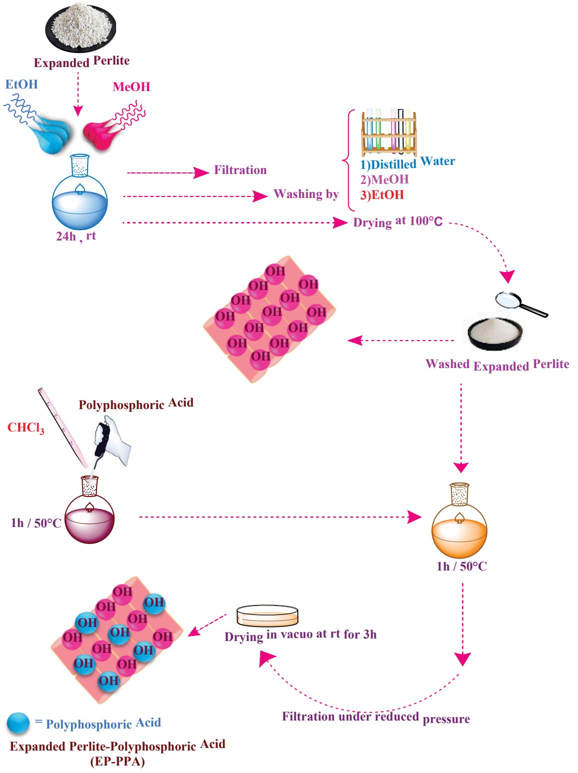
One of these new methods is to run reactions on the surface of heterogeneous catalysis due to easy recovering and possible recycling of the catalyst, simple experimental procedures, mild reaction conditions and minimization of chemical wastes as well. Moreover, the reaction on the surface of heterogeneous catalyst is more convenient to run, or a higher yield of product is attained than a solution counterpart.

Raw Perlite as a naturally occurring glassy volcanic rock, upon vaporization of water trapped in its structure

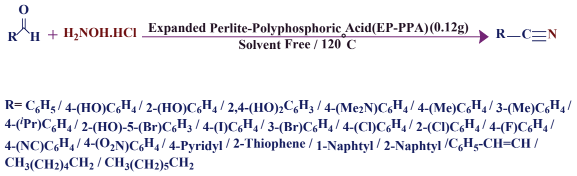
(700–1200 °C), expands up to 10–20 times of its initial volume which is then called "Expanded Perlite".[93] Expanded Perlite with high porosity, strong absorbability, thermal and chemical stability, as well as low toxicity, low cost, non-corrosiveness and ease of handling mainly consists of silica and alumina (Table 1).[94–101] Moreover, it finds a noteworthy role as catalyst or excellent support in some organic reactions or in the preparation of heterogeneous catalysts along in many industries.[101–113] Polyphosphoric acid (PPA) as an efficient protic acid catalyzed numerous organic reactions.[114–116] However, the viscous nature of PPA has limited its application in synthetic organic reactions.

Intrinsic drawbacks of homogeneous acid catalysis (as an important area of organic synthesis and vital industrial significance)[117] have encouraged the research to replace homogeneous acid catalysts by recyclable solid acids. During the course of our studies aimed at developing heterogeneous acid catalysts Fe_3O_4@WO_3-EAE-SO_3H,[118] HAP@AEPH_2-SO_3H,[119,120] are being utilized as replacement of homogeneous acids in synthetic organic reactions. Also, to overcome the difficulty of PPA handling (due to its viscosity), recently the authors reported the preparation of Expanded Perlite-Polyphosphoric Acid (EP-PPA) (from commercially available chemicals) according the multiple steps manner in Scheme 1. At first, to remove organic impurities finely powdered expanded perlite was stirred in a 1 : 1 (*v* / *v*) mixture of methanol and ethanol at room temperature for 24 h. The resulting suspension was filtered and washed in turn by distilled water, methanol and ethanol. The grey resulting expanded perlite powder was dried at 100 °C for 3 h.[102] Thereafter, Expanded Perlite was added to a solution of polyphosphoric acid in $CHCl_3$ with vigorous stirring at 50 °C. After 1 h, $CHCl_3$ was removed under reduced pressure before drying the resulting Expanded Perlite-Polyphosphoric Acid (EP-PPA) *in vacuo* at room temperature for 3 h. The successfully synthesized EP-PPA has been used as a green and efficient heterogeneous acid catalyst for synthesis of aryl/alkylbis(indolyl)methanes through the one-pot reaction of indole and carbonyl compounds, in water.[101]

With an intention of searching new mild synthetic methodologies in organic chemistry[121,122] herein we report an efficient protocol for direct transformation of aldehydes into nitriles using Expanded Perlite-Polyphosphoric Acid (EP-PPA) that furnishes the products in excellent yields (Scheme 2).



Scheme 1. The schematic pathway for synthesis of Expanded Perlite-Polyphosphoric Acid (EP-PPA).



Scheme 2. Expanded Perlite-Polyphosphoric Acid (EP-PPA) catalyzed conversion of aldehydes into nitriles under solvent-free conditions.

EXPERIMENTAL

General

All chemical reagents and solvents were purchased from Merck Chemical Company and were used as received without further purification. The purity determination of the products and the progress of the reactions were monitored by TLC (Thin Layer Chromatography) on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR (Fourier Transform Infrared) spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer. The NMR (Nuclear Magnetic Resonance) spectra were recorded on Brucker Avance 300, 400 and 600 MHz instruments in $CDCl_3$ and DMSO-d_6. Mass spectra were recorded with a Shimadzu GC-MS-QP5050 and CH7A Varianmat Bremem instrument at 70 eV, in m / z (rel %). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out on a 76004555 SPECTRO ARCOS ICP-OES analyzer. SEM images were recorded using a Leo1450 VP scanning electron microscope equipped with an SC7620 energy-dispersive X-ray spectrometer (EDX), presenting a 133 eV resolution at 20 kV. The chemical compositions of the expanded perlite were specified with X-ray fluorescence spectroscopy (XRF), using BRUKER axs-S4 EXPLORER spectrometer. All the yields refer to isolated products after purification by thin layer chromatography.

Preparation of the Catalyst

PRE-PREPARATION OF EXPANDED PERLITE

Expanded Perlite was obtained from Iran Birjand resources. Before use and characterization, Expanded Perlite (10 g) was finely powdered and put into 400 mL methanol and ethanol (1 : 1 *v* / *v*). To remove the pollution and organic components, the mixture was stirred at room temperature for 24 h. The resulting suspension was filtered and washed in turn by distilled water, methanol and ethanol three times respectively. The grey resulting Expanded Perlite powder was dried at 100 °C for 3 h.[102]

PREPARATION OF EXPANDED PERLITE-POLYPHOSPHORIC ACID (EP-PPA)

A mixture of polyphosphoric acid (2.1 g) in $CHCl_3$ (100 mL) was stirred at 50 °C for 1 h. Expanded Perlite (4.9 g) was added to the resulting solution and the mixture was stirred vigorously. After 1 h, $CHCl_3$ was removed under reduced pressure and the resulting Expanded Perlite-Polyphosphoric Acid (EP-PPA) was dried *in vacuo* at room temperature for 3 h.[101]

Typical Procedure for Direct Preparation of Benzonitrile from Benzaldehyde using Expanded Perlite-Polyphosphoric Acid (EP-PPA)

A mixture of finely powdered hydroxylamine hydrochloride (3 mmol, 0.208 g) and benzaldehyde (1mmol, 0.106 g) was ground together in a mortar using a pestle for 3 min. Then, Expanded Perlite-Polyphosphoric Acid (EP-PPA) (0.12 g) was added to the resultant mixture and the reaction (under solvent-free condition) was allowed to proceed under magnetic stirring and heating at 120 °C. After the completion of the reaction, which was monitored by TLC (*n*-hexane : ethyl acetate = 4 : 1), the reaction mixture was cooled to room temperature and diluted with ethyl acetate (5 mL). Afterwards, the catalyst was separated by centrifugation, washed with ethyl acetate 3 times and dried at 50 °C for use in the next run. Then the crude reaction mixture was poured into distilled water (5mL) and neutralized by sodium bicarbonate. The organic layer was dried over sodium sulfate. After evaporation of the solvent, the residue was purified by thin-layer chromatography on silica gel using *n*-hexane : ethyl acetate (4 : 1) as eluent to yield the desired benzonitrile (0.0976 g, 95 %).

RESULTS AND DISCUSSION

Characterization of Expanded Perlite-Polyphosphoric Acid (EP-PPA)

Based on X-ray fluorescence analysis (XRF) SiO_2 and Al_2O_3 are the main components of Expanded Perlite (Table 1). Consequently, expanded perlite is considered as a natural alumino-silicate.[102]

To verify the structure of Expanded Perlite and Expanded Perlite-Polyphosphoric Acid (EP-PPA) Fourier transform infrared (FT-IR) spectroscopy was utilized. Five main absorption bands at 3443 cm^{-1}, 1626 cm^{-1}, 1054 cm^{-1}, 791 $cm^{-1}$and 460 cm^{-1}were observed in Figure 1a.[123] The bands at 3443 cm^{-1} and 1626 cm^{-1} are related to the stretching and bending modes of the hydroxyl groups which are attached to the surface of Expanded Perlite (mainly Si–OH groups) and the adsorbed water molecules.[106] The Si-O stretching vibrations of Si-O-Si and Si-O-Al were shown by the absorption bands around 1054 cm^{-1} and 791 cm^{-1} respectively.[124] Also, vibrational bending of Si-O-Si was observed at about 460 cm^{-1}.[123]

As it is evident from Figure 1b, P-O stretching vibration of polyphosphoric acid was appeared at about 1043–977 cm^{-1}.[125–127] The absorption band at about 1220–1135 cm^{-1} could be attributed to stretching vibration of P=O bond.[125–127] Moreover, the broad band around

Table 1. The chemical composition of Expanded Perlite based on XRF analysis.

Constituent	SiO_2	Al_2O_3	K_2O	Fe_2O_3	Na_2O	CaO	MgO
Percentage	75.22	12.77	5.18	0.74	2.52	0.60	0.22
Constituent	BaO	SO_3	ZrO_2	TiO_2	Rb_2O	SrO	MnO
Percentage	0.08	0.06	0.01	0.11	0.01	0.01	0.06

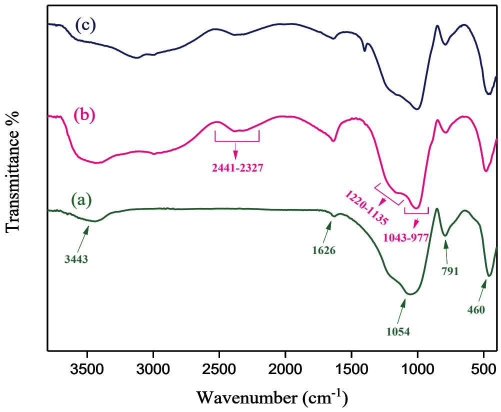


Figure 1. FT-IR spectra of the Expanded Perlite (a), Expanded Perlite-Polyphosphoric Acid (EP-PPA) (b), 6th reused Expanded Perlite-Polyphosphoric Acid (EP-PPA) (c).

2441–2327 cm^{-1} indicated the P-O-H stretching modes.[125–127] Furthermore, the incorporation of polyphosphoric acid on the surface of Expanded Perlite can be verified by increasing the intensity of O-H stretching vibration.[101]

Scanning electron microscopy (SEM) shows the structure and morphology of the Expanded Perlite and Expanded Perlite-Polyphosphoric Acid (EP-PPA). According the SEM images the layered porous structure of Expanded Perlite preserved after the immobilization of Polyphosphoric acid on its surface.[101]

The energy dispersive X-ray spectroscopy (EDX) of Expanded Perlite in good agreement with the XRF results indicates the main elemental components of the Expanded Perlite. Additionally, the successful immobilization of Polyphosphoric acid on Expanded Perlite was confirmed by the existence of P element in the EDX analysis of Expanded Perlite-Polyphosphoric Acid (EP-PPA).[101]

The number of acidic sites in Expanded Perlite-Polyphosphoric Acid (EP-PPA) was determined by back-titration analysis of the catalyst. To a solution of sodium hydroxide (0.1 M, 15 mL) 100 mg of the catalyst was added and stirred at room temperature. After 24 h, the resulting suspension was filtered. The filtrate was neutralized using a standard solution of HCl (0.1 M). The consumed volume of HCl (9 mL) to reach the equivalence point of titration determined the amounts of acidic sites per 1.000 g of Expanded Perlite-Polyphosphoric Acid (EP-PPA) (3.75 mmol g^{-1} of catalyst). Additionally, based on ICP-OES analysis, the total amount of grafted P was calculated to be 2.28 mmol g^{-1}, which is in good agreement with that evaluated by pH analysis.

Catalytic Conversion of Aldehydes into Nitriles

In the present study, direct conversion of aldehydes into nitriles has been designed and realized *via* the formation of the corresponding oximes, using hydroxylamine hydrochloride in conjunction with Expanded Perlite-Polyphosphoric Acid (EP-PPA) without isolation of the oxime intermediates (Scheme 2). In our preliminary experiments, to achieve the maximum yield and efficiency, the reaction conditions (applying various amounts of catalyst, temperatures, solvents as well as different molar ratios of benzaldehyde / hydroxylamine hydrochloride) were established using benzaldehyde as the model substrate. The obtained results are summarized in Table 2. At the outset, the reaction of benzaldehyde (1 mmol) with hydroxylamine hydrochloride (3 mmol) was studied at 120 °C in the absence of any catalyst and solvent. A trace amount of benzonitrile was produced even after 24 h (Table 2, entry 1). Formation the corresponding product in the presence of Expanded Perlite-Polyphosphoric Acid (EP-PPA) (0.16 g) (Table 2, entry 2) confirmed the role of Expanded Perlite-Polyphosphoric Acid (EP-PPA) as a solid acid catalyst in direct conversion of aldehydes into nitriles. Interestingly, the same result was gained by performing the reaction in DMF (Table 2, entry 3). With respect to the importance of green chemistry legislations (elimination of solvents in the chemical processes),[128] subsequent experiments were conducted in solvent-free conditions. Next, we address optimization in terms of the reaction temperature. Performing the model reaction at lower temperatures decreased the yield of desired product (Table 2, entries 4–7). To improve the performance of the reaction, the influence of different amounts of catalyst was studied on model reaction (Table 2, entries 8–11). No improvement in the yield and reaction rate was observed by increasing the catalyst loading up to

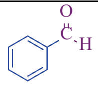
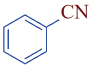
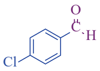
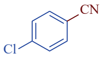
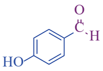
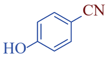
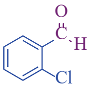
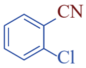
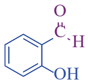
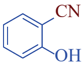
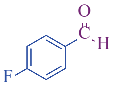
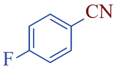
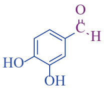
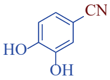
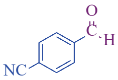
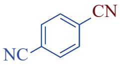
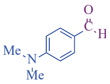
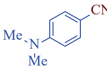
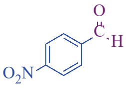
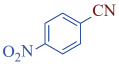
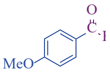
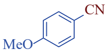
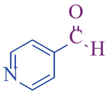
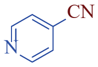
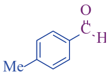
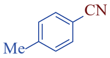
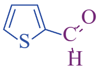
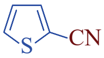
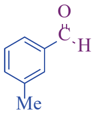
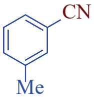
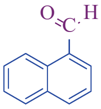
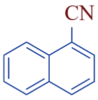
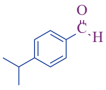
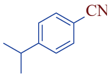
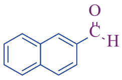
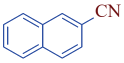
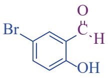
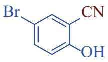
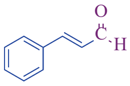
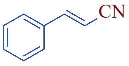
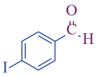
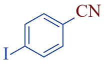
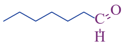
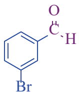
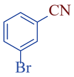
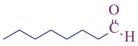
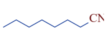
Table 2. Optimization of reaction conditions for direct conversion of benzaldehyde into benzonitrile using Expanded Perlite-Polyphosphoric Acid (EP-PPA).

Entry	Molar ratio Benzaldehyde / $H_2NOH.HCl$	m(catalyst) / g	Solvent	Temperature / °C	Time / min	Conversion / %
1	1 : 3	–	–	120	24(h)	trace
2	1 : 3	0.16	–	120	28	100
3	1 : 3	0.16	DMF	120	35	100
4	1 : 3	0.16	–	115	38	100
5	1 : 3	0.16	–	110	4(h)	100
6	1 : 3	0.16	–	105	24(h)	70
7	1 : 3	0.16	–	100	24(h)	50
8	1 : 3	0.2	–	120	20	100
9	**1 : 3**	**0.12**	**–**	**120**	**28**	**100**
10	1 : 3	0.1	–	120	38	100
11	1 : 3	0.08	–	120	40	100
12	1 : 2	0.12	–	120	40	100
13[(a)]	1 : 3	0.12	–	120	2.5(h)	20
14[(b)]	1 : 3	0.12	–	120	40	75
15[(b)]	1 : 3	0.1	–	120	60	65
16[(b)]	1 : 3	0.08	–	120	85	50
17[(b)]	1 : 3	0.06	–	120	3.5(h)	50
18[(b)]	1 : 3	0.04	–	120	6(h)	30
19[(b)]	1 : 3	0.02	–	120	10(h)	15

[(a)] The reaction was performed in the presence of Expanded Perlite.

[(b)] The reaction was performed in the presence of polyphosphoric acid.

Table 3. Direct conversion of various aldehydes into nitriles using Expanded Perlite-Polyphosphoric Acid (EP-PPA) under optimized reaction conditions.

Entry	Aldehyde	Product	Time / min	Conversion / %	Isolated yield / %	Entry	Aldehyde	Product	Time / min	Conversion / %	Isolated yield / %
1			28	100	95	13			35	100	96
2			13	100	97	14			50	100	91
3			17	100	94	15			51	100	95
4			19	100	96	16			33	100	93
5			20	100	98	17			35	100	95
6			13	100	93	18			43	100	92
7			15	100	95	19			40	100	97
8			25	100	92	20			50	100	94
9			22	100	93	21			38	100	93
10			34	100	97	22			40	100	95
11			35	100	95	23			28	100	92
12			40	100	92	24			36	100	96

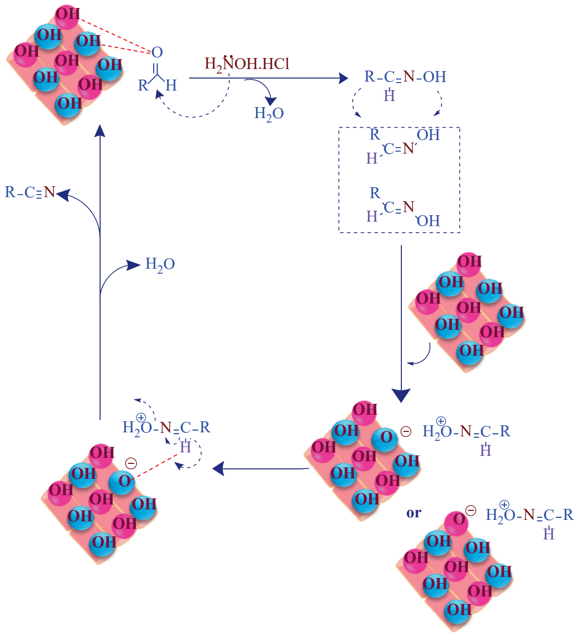
0.2 g. Following experiments led to the finding that a reasonable yield of desired product can be gained using 0.12 g of Expanded Perlite-Polyphosphoric Acid (EP-PPA). In the course of our research and evaluation of different molar ratio of benzaldehyde/hydroxylamine hydrochloride we have found that best yield of desired product was afforded using 1/3 molar ratio of benzaldehyde / hydroxylamine hydrochloride (Table 2, entry 12).

Succeeding, to further check the true catalyst species in direct conversion of aldehydes into nitriles, in separate flasks the model reaction was performed under the identical conditions in the presence of Expanded Perlite and different amounts of polyphosphoric acid (Table 2, entries 13–19). As shown in Table 2, the reaction did not occur efficiently and the desired product was scarcely obtained.

Further, based on the above-optimized conditions (Table 2, entry 9) the scope of this transformation was evaluated for structurally diverse aldehydes. Several aryl aldehydes including (electron-donating and electron-withdrawing groups), hetero-aromatic aldehydes, naphthaldehydes as well as α,β-unsaturated and aliphatic aldehydes were transformed smoothly into the corresponding nitriles *via* this protocol in high yields. The results are summarized in Table 3. The results indicated that the conversion time of reaction depends on the aldehydes, the positions and electron-donating or electron-withdrawing nature of the substituents on the reactants. In comparison, heteroaromatic aldehydes and naphthaldehydes show lower reactivity than benzaldehyde (Table 3, entry 1 *vs.* entries 18–21). As illustrated in Table 3, the aldehydes with electron-donating substituents were more reactive than those with electron-withdrawing groups (Table 3, compare entries 1–9 with entries 10–17). It was evident that due to steric hindrance *ortho*- substituted aldehydes show lower reactivity than *p*-substituted ones (Table 3, entry 2 *vs.* entry 3, entry 13 *vs.* entry 14).

In the present study, the progress of the reaction was monitored by the disappearance of the starting material (aldehyde and then aldoxime) and further formation of the desired nitrile compound on TLC. In the following the appearance of a strong sharp absorption band at 2207–2246 cm^{-1} due to CN group of nitriles as well as the disappearance of stretching frequencies of C=O, −CHO, OH and C=N in the FT-IR spectrum confirmed the completion of the reaction. All of the synthesized products were known compounds and their physical properties (color, melting points), FT-IR spectroscopy, mass spectrometry found to be identical with those of authentic samples. Based on mass spectra the observed molecular ion peaks (M$^+$) were in good agreement with the excepted molecular weights. Moreover, the chemical structure of the purified compounds was recognized by ^{1}HNMR and ^{13}CNMR spectroscopy. A resonating signal at around 114–120 ppm assigned the quaternary carbon of nitrile (See the supporting information for details).

The overall reaction mechanism for direct transformation of aldehydes into nitriles is described in Scheme 3. Based on the obtained results under the acidic conditions, the reaction proceeds *via* the formation of aldoxime. Aldehydes converted into oximes rapidly irrespective of the electronic nature of the aldehydes, whereas the electronic nature of the aldehydes has an outstanding effect on dehydration step. Oximes with high electron density afforded the corresponding nitriles rapidly, but all of the substrates with low electron density needed a longer reaction time. This idea is supported by the data evident from Table 3. Dehydration step at 120 °C was facilitated by the protonation of the hydroxy group in the presence of solid acid catalyst converting this moiety to a better leaving group. Subsequently, the solid acid (Expanded Perlite-Polyphosphoric Acid (EP-PPA)) regenerated and re-entered the catalytic cycle by providing the active sites for further turnovers. This proposed mechanism was supported by the previous reports.[91]



Scheme 3. Plausible mechanism for direct conversion of aldehydes into nitriles in the presence of Expanded Perlite-Polyphosphoric Acid (EP-PPA).

From the perspective of "green chemistry", recycling and reusability of the catalyst renders the chemical processes truly eco-friendly green protocols. In this regard, reusability of Expanded Perlite-Polyphosphoric Acid (EP-PPA) as a solid acid catalyst was assessed in direct transformation of benzaldehyde into benzonitrile. At the end of reaction (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with ethyl acetate (5 mL). Afterwards, the catalyst was separated by centrifugation, washed with ethyl acetate 3 times and dried at 50 °C for use in the next run. The recycling efficiency has been tabulated in Table 4. According the result of Table 4, a negligible decrease in the conversion and yield was observed after 6 successive recycle runs, due to efficient catalytic activity and long term-durability of Expanded Perlite-Polyphosphoric Acid (EP-PPA) in direct transformation of benzaldehyde into benzonitrile. Any structural changes of Expanded Perlite-Polyphosphoric Acid (EP-PPA) after 6 runs in direct transformation of benzaldehyde into benzonitrile was investigated by FT-IR spectroscopy and ICP-OES analysis. FT-IR spectrum of the 6th reused Expanded Perlite-Polyphosphoric Acid (EP-PPA) showed no significant changes in frequencies, intensities and shapes of absorption bands (Figure 1c). ICP analysis shows that freshly prepared Expanded Perlite-Polyphosphoric Acid (EP-PPA) contains 2.28 mmol of P per 1.000 g catalyst, while the Expanded Perlite-Polyphosphoric Acid (EP-PPA) after six cycles contains 1.87 mmol of P per 1.000 g of catalyst.

In the present study, to determine the homogeneity/heterogeneity nature of Expanded Perlite-Polyphosphoric Acid (EP-PPA), we introduced a hot filtration test in direct conversion of aldehydes into nitriles. Toward this point, the model reaction was studied under the optimal conditions. After 50 % conversion to product (14 min), the solid catalyst was separated from the reaction mixture by filtration. Then, the reaction was permitted to continue without catalyst for a further 14 min. No increase in the amount of product was observed even after an extended time, as the reaction progress was followed by thin layer chromatography. Based on ICP-OES and back-titration analysis negligible amounts of active species (less than 0.09 mol% of the total amount of grafted P and 12 % of acidic sites per 1.000 g of Expanded Perlite-Polyphosphoric Acid (EP-PPA)) leached out from the solid support during the hot filtration test in direct conversion of aldehydes into nitriles. The obtained results clearly established the strong attachment of polyphosphoric acid to the surface of Expanded Perlite. In other words, insignificant amount of H^+ in reaction mixture did not have a considerable effect on the reaction progress and a notable increase in the reaction yield could be attributed to the heterogeneous appended polyphosphoric acid to the surface of Expanded Perlite (Figure 2).

In order to further explore the possibility of the heterogeneous nature of catalyst two different experiments (pH measuring and ^{31}P-NMR spectroscopy) were also investigated on the model reaction. To this end, the model reaction was performed under the optimal conditions in the absence of hydroxylamine. After separating the catalyst by centrifugation and washing it with distilled water the pH was measured to be 5.9. It means that no obvious

Table 4. Direct transformation of benzaldehyde into benzonitrile in the presence of the reused Expanded Perlite-Polyphosphoric Acid (EP-PPA).

Run	Time / min	Conversion / %
1	28	100
2	28	100
3	28/35	95/100
4	28/37	95/100
5	28/40	80/100
6	28/50	75/100

The first number in the third column corresponds to conversion after 28 min.

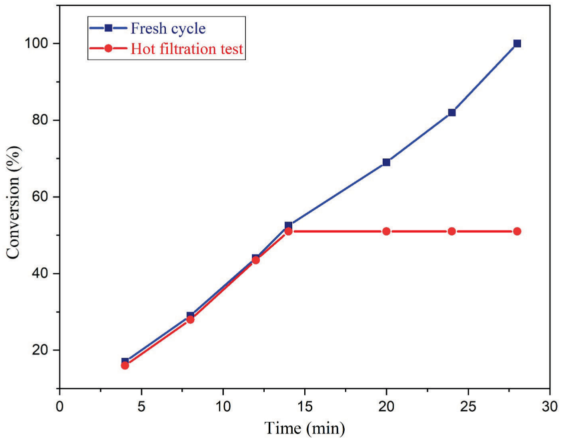


Figure 2. Time-dependent correlation of the product yield in hot filtration test.

Table 5. Comparison of the catalytic activity of Expanded Perlite-Polyphosphoric Acid (EP-PPA) with some literature precedents in direct transformation of benzaldehyde into benzonitrile.

Entry	Catalyst	Amount of catalyst / g	Solvent	Temperature / °C	Time / min	Reusability	Yield / %	Ref.
1[(a)]	HCl. DMPU	0.5mmol	CH_3CN	60	4 h	–	98	[56]
2	–	–	NMP	115	5 h	–	86	[62]
3	Peroxymonosulfate-alumina /MW	0.61 : 1	–	r.t.	7.5	–	77	[90]
4	KF/Al_2O_3	7.25	DMF	100	5 h	–	77	[51]
5	Graphite/ $MeSO_2Cl$	0.1 : 0.08 mL	–	100	90	–	90	[58]
6	Dry Al_2O_3/ $MeSO_2Cl$	0.5 : 0.075 mL	–	100	25	–	90	[49]
7	Choline Chloride-Urea/ MW	15 mol%	–	100	12 h	5	92	[92]
8[(b)]	Dry CSMIL	0.015	–	70	90	5	93	[83]
9[(c)]	HAP@AEPH$_2$-SO$_3$H	0.08	DMF	120	120	5	75	[91]
10	EP-PPA	0.12	–	120	28	6	95	Present study

[(a)] DMPU: *N,N'*-Dimethylpropyleneurea.

[(b)] CSMIL: Chitosan supported magnetic ionic liquid.

[(c)] HAP@AEPH$_2$-SO$_3$H: Sulfonated nano hydroxyapatite functionalized by 2-aminoethyl dihydrogen phosphate.

hydrolyzing of appended polyphosphoric acid was happened. In other words, the H$^+$ concentration in solution is presumably very small. Alternatively, after dispersion the separated catalyst in D_2O, ^{31}P-NMR spectroscopy of the filtrate was recorded to determine the presence of P in solution. Interestingly, ^{31}P-NMR spectrum exhibited that a negligible amount of appended polyphosphoric acid was hydrolyzed (*"See Supporting Information" file, Fig S 89*). According to the obtained results, the conclusion could be derived that the heterogeneous Expanded Perlite-Polyphosphoric Acid (EP-PPA), is the catalyst promoter in this reaction.

To obtain deeper insight into the performance of Expanded Perlite-Polyphosphoric Acid (EP-PPA) in direct transformation of benzaldehyde into benzonitrile, the results of the present study were compared with some of those reported previously in the literature (Table 5). Although, each of the listed catalysts in Table 5 are valuable with their own advantages, however, the present methodology is much superior to almost all of them in terms of reaction media, (Table 5, entries 1, 2, 4 and 9) reaction time, (Table 5, entries 1, 2, 4, 5 and 7–9) as well as using heterogeneous catalyst with easy work-up procedure (Table 5, entries 1–6). Moreover, this solid acid catalyst is comparable in terms of price, non-toxicity and ease of separation.

CONCLUSION

In the present study, the authors attempted to expand the application of Expanded Perlite-Polyphosphoric Acid (EP-PPA) as an efficient, eco-friendly, non-hazardous, nonexplosive, easy to handle, chemically stable and heterogeneous catalyst in organic reactions. In this regards, direct transformation of aldehydes into nitriles using the above-mentioned catalyst under solvent-free condition is reported. The method has been applied for direct transformation of structurally different aromatic aldehydes (including electron-donating and electron-withdrawing groups), hetero-aromatic aldehydes, naphthaldehydes as well as α,β-unsaturated and aliphatic aldehydes into respective nitriles in excellent yields. The notable features of the present approach are simple procedure, short reaction times, high yields of products as well as green reaction media and very wide range of substrates. Additionally, the excellent recycling capability of catalyst (up to six runs without any appreciable loss in its catalytic efficiency) is another advantage of the present protocol compared with traditional methods for the synthesis of titled compounds.

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Supplementary Information. Supporting information to the paper is attached to the electronic version of the article at: https://doi.org/10.5562/cca3980.

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