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Nano kaolin-SO_3H as a new efficient and reusable catalyst for one-pot synthesis of 2,4,5-trisubstituted imidazoles in solvent-free conditions

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KEYWORDS
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Nanoparticles;
Heterogeneous catalyst;
Solvent-free;
Tri-substituted imidazole.

Abstract. Nano kaolin-SO_3H as a new reusable and green heterogeneous catalyst was prepared by the reaction of kaolin nanoparticles with chlorosulfonic acid. This new type of solid acid, which contains the properties of a Lewis acid (Al^{3+}) and a BrØnsted acid (SO_3H group), was characterized by FT-IR, XRD, SEM, TEM, XRF, EDS, and TGA. Nano kaolin-SO_3H was used as a recoverable acidic heterogeneous catalyst for one-pot synthesis of 2,4,5-trisubstituted imidazoles *via* three-component condensation of 1,2-diketones, various aromatic aldehydes, and ammonium acetate. Short reaction time, simple workup, high yields, solvent-free conditions, and environmental friendly catalysts are some advantages of this protocol.

1. Introduction

Multi-substituted imidazoles are important compounds in nature. Due to the widespread use of this class of heterocyclic compounds in the pharmaceutical industries and agriculture, to resist composition and fluorescent brighteners on textile, optical, and photographic materials, many chemists have turned to the preparation of these compounds [1-5]. Recently, the synthesis of imidazoles has been carried out in ways that are affordable and environmental friendly [6].

Due to the toxic nature of many organic solvents such as chloroform and carbon tetrachloride, it is suggested to design processes that are rooted in green chemistry [7,8]. Multi-Component Reactions (MCRs) are one-pot processes used for the synthesis of new organic and, especially, medicinal compounds [9-11]. The advantages of these classes of reactions include short response time, high efficiency, clean workup, and easy purification. Many of these reactions are done in solvent-free conditions. To date, several reports have been presented on the synthesis of 2,4,5-trisubstituted imidazoles using catalysts such as nano Fe_3O_4@SiO_2-OSO_3H [3], L-Proline [12], montmorrilonite K10 and nano sulfated zirconia [13], zeolite and [EMIM]OAc [14] silica phosphoric acid [15], silicagel/$NaHSO_4$ [16], $HClO_4$-SiO_2 [17], $BF_3.SiO_2$ [18], $K_5CoW_{12}O_{40}.3H_2O$ [19], silica-bonded S-sulfonic Acid [20], mercaptopropylsilica [21], MCM-41 or p-TsOH [22], silica-bonded propylpiperazine *N*-sulfamic acid [23], sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl]ester [24], and Morpholinium Hydrogen Sulphate [25].

Kaolin (hydrated aluminum silicate) with chemical composition $Al_2Si_2O_5(OH)_4$ is an industrial mineral formed by the decomposition of feldspar. The primary structural unit of this group is a layer composed of one alumina octahedral sheet condensed with one silicate tetrahedral sheet through oxygen atoms. Rocks that are rich in kaolinite are known as kaolin or china clay [26]. The name kaolin derives from the Chinese

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origin and means high ridge. High ridge is a reference to the hills in the southeastern china where the clay was originally discovered and used [27]. Kaolin was used commercially in pharmaceutical and agricultural fields for hundreds of years. The primary and largest use is in the production of paper including the gloss on some grades of coated paper. Its color, gloss, and hardness are ideal characteristics for such products. Kaolinite is one of the most common minerals. Large volumes of kaolinite clays are used for the production of cement, ceramics, bricks, and porcelain [28,29]. The greatest demand for kaolinite is in the paper industry to produce high-quality paper [30].

Nano kaolin-SO_3H as a new reusable and green heterogeneous nanocatalyst was prepared by the reaction of kaolin nanoparticles with chlorosulfonic acid. It could be an efficient solid acid catalyst for the promotion of many organic reactions [31]. During the course of our studies on the development of green chemistry, an environmentally benign procedure was designed for the one-pot synthesis of 2,4,5-trisubstituted imidazole derivatives under thermal and solvent-free conditions using nano kaolin-SO_3H as a new efficient and reusable catalyst.

In a simple procedure, a mixture of 1,2-diketone (1 mmol), an aldehyde (1 mmol), and ammonium acetate (6 mmol) is condensed in the presence of nano kaolin-SO_3H (0.05 g) as a solid catalyst for 7-35 minutes under conventional heating conditions at 140°C in the absence of solvent (Scheme 1).

2. Experimental section

2.1. Materials and apparatus

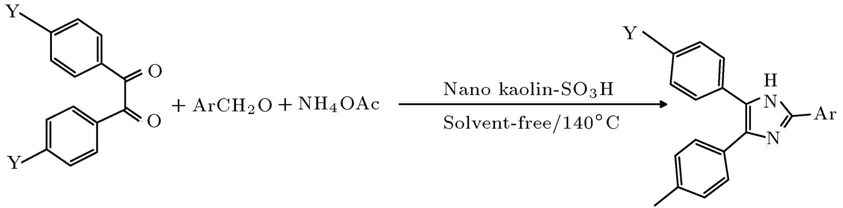
Chemicals such as 1-2-diketones, ammonium acetate, aldehyde derivatives, chlorosulfonic acid, ethanol, and acetone were purchased from Fluka, Merck, and Aldrich chemical companies. Kaolin is an industrial mineral derived from the tile industry. Some of imidazole products are known compounds characterized by comparison of their spectral data (^{1}H-NMR, IR), TLC, and physical data with authentic samples. New products were characterized also by CHN analysis. ^{1}H and ^{13}C NMR spectra were recorded on an Avance BRUKER (DRX-400 MHz) in acetone-d_6 or DMSO-d_6 as a solvent. UV-V is spectra were taken by a double-beam Perkin-Elmer 550S spectrophotometer in the range of 200-400 nm, using acetone as the solvent. IR spectra were determined on a Nicolet Magna series FTIR 550 spectrometer using KBr pellets. The elemental analyses (C, H, and N) were obtained from a Carlo ERBA Model EA 1108 analyzer carried out on a Perkin-Elmer 240C analyzer. Thin Layer Chromatography (TLC) on commercial plates of silicagel 60 F_{254} was used to monitor the progress of the reactions. XRD patterns were collected on a Philips Xpert MPD diffractometer equipped with a Cu Kα anode ($\lambda = 1.54$ Å) in the 2θ range of 10 to 80°. Elemental composition was investigated by XRF BRUKER S4 EXPLORER. The average size of kaolin-SO_3H nanoparticles was analyzed by TEM using a Philips CM120 with a LaB6 cathode and accelerating voltage of 120 kV. Energy-Dispersive X-ray Spectroscopy (EDS) of catalyst was measured by the EDS instrument, Phenom pro X.

2.2. Preparation of nano kaolin-SO_3H

In a ventilated cabinet, a suction flask of 100 mL containing 5 g of commercial kaolin nanoparticles was equipped with a dropping funnel containing 20 mL of chlorosulfonic acid and gas inlet tube for conducting obtained HCl gas over a water vessel. Then, 25 mL of chloroform was added to the suction flask and chlorosulfonic acid was added drop-wise to the mixture with vigorously mixing at room temperature. After the addition of chlorosulfonic acid, a white solid was obtained. The solid was filtered and washed with chloroform and dried at room temperature. Finally, 5.6 g of nano kaolin-SO_3H was obtained and characterized by FT-IR, XRD, SEM, TEM, XRF, TGA, and EDS techniques.

2.3. General procedure for the preparation of 2,4,5-trisubstituted imidazoles

In order to achieve satisfactory results, in a typical experiment, a mixture of aromatic aldehyde (1 mmol), 1,2-diketone (1 mmol), ammonium acetate (6 mmol), and nano kaolin-SO_3H (0.05 g) was stirred in a test tube for 7-35 minutes in a conventional heating condition at 140°C. After completion of the reaction, the reaction mixture was cooled to room temperature and was washed with acetone (3×5 mL). The product was separated from the catalyst by filtration and



Scheme 1. One-pot synthesis of 2,4,5-trisubstituted imidazole derivatives.

after evaporation of the solvent, the pure product was obtained.

2.4. *Spectroscopic data for selected compounds*

Bis[3-hydroxy-4,5-diphenylimidazole-yl]methane (18):
Brown solid. mp/°C: 244-247. $\lambda_{\max}$ ($CHCl_3$)/nm: 333 ($\pi \rightarrow \pi^*$), 218 ($n \rightarrow \pi^*$). $\bar{\upsilon}$ (KBr)/cm^{-1} 3500-3100 (N-H), 3052 (=C-H), 2922 (-C-H), 1604-1400 (C=C and C=N), 1442 (CH_2 bending), 1260 (Ar-O), 765 and 695 (=C-H bending OOP of monosubstituted phenyl rings). ^{1}H NMR (Acetone-d_6)/ppm: δ_H = 13.05 (2 H, s, NH), 12.79 (2 H, s, OH), 7.97 (2 H, s), 7.5-7.0(20 H, m), 6.92 (2 H, d, $^3J_{HH}$ = 8.0 Hz), 6.60 (2 H, d, $^3J_{HH}$ = 8.0 Hz). ^{13}C NMR (Acetone-d_6)/ppm: δ_C = 153.07, 136.19, 136.08, 131.80, 130.66, 129.05, 127.76, 126.32, 124.24, 123.38, 120.08, 115.67, 41.70. Anal. Calcd.: for $C_{43}H_{32}N_4O_2$ (%): C 81.132, H 5.031, N 8.805. Found: C 84.89, H 5.069, N 8.807.

2-(4-N,N-dimethylaminophenyl)4,5-di(4-flourophenyl -1H-imidazole (19):
Off-white solid. mp/°C: 269-271. $\lambda_{\max}$ (Acetone)/nm: 285 ($\pi \rightarrow \pi^*$), 245 ($n \rightarrow \pi^*$). $\bar{\upsilon}$ (KBr)/cm^{-1}: 3397 (N-H), 3066 (=C-H), 2912 (-C-H), 1649-1400 (C=C and C=N), 1363 (CH_3 bending), 1221 (C-N), 1221 (Ar-F), 835 (=C-H bending OOP of parasubstituted phenyl rings). ^{1}H NMR (Acetone-d_6)/ppm: δ_H = 12.35 and 11.978 (1H, s, NH), 7.87 (2 H, d, $^3J_{HH}$ = 8.4 Hz), 7.495 (4 H, t, $^3J_{HH}$ = 6.8 Hz, $^3J_{HF}$ = 6.8 Hz), 7.199 (4 H, t, $^3J_{HH}$ = 6.8 Hz, $^4J_{HF}$ = 5.6 Hz), 6.77 (2 H, d, $^3J_{HH}$ = 8.4 Hz), 2.970 (6 H, s). ^{13}C NMR (Acetone-d_6)/ppm: δ_C = 172.52, 162.00 (d, $^1J_{C-F}$ =245.0 Hz), 150.77, 146.94, 130.6 (d, $^3J_{C-F}$ =8.0 Hz), 126.76, 118.52, 115.82 (d, $^2J_{C-F}$ =20.0 Hz), 112.35, 100.01, 21.51. Anal. Calcd.: for $C_{23}H_{18}N_3F_2$ (%): C 73.60, H 5.061, N 11.20. Found: C 73.26, H 5.311, N 11.678.

3. Results and discussion

3.1. *Characterization of nano kaolin-SO_3H*

To prove the SO_3H group on the catalyst, the FT-IR (ATR) spectra of kaolin nanopaticles and kaolin-SO_3H nanoparticles were compared (Figure 1). In FT-IR spectrum of kaolin, many bands at 3686 and 3620, 1114, 990, 909, 791, and 752 cm^{-1} existed. However, in the nano kaolin-SO_3H, in addition to the above-mentioned bands, a band at 1160 cm^{-1} and a very broad band at 2700-3400 cm^{-1} appeared. The broad band at 1160 cm^{-1} and a very broad band at 2700-3400 cm^{-1} verified the O=S=O and -SO-H vibrations on nano kaolin-SO_3H, respectively.

TGA-DTG curves of kaolin display a strong peak at 517°C, which is due to dehydroxylation of kaolin within the 450-600°C temperature range, resulting in a weight loss of 15.34% and formation of metakaolin.

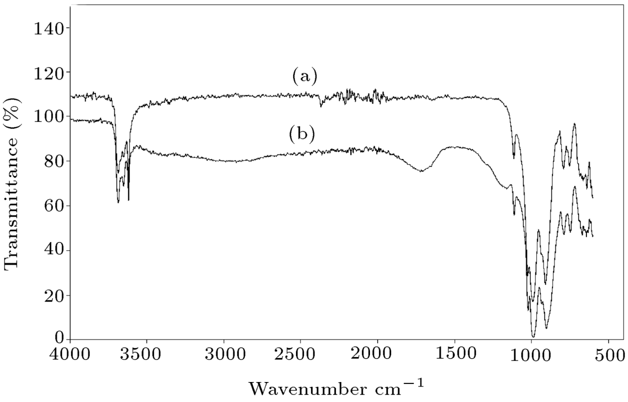


Figure 1. FT-IR (ATR) spectra of (a) kaolin nanopaticles and (b) nano kaolin-SO_3H.

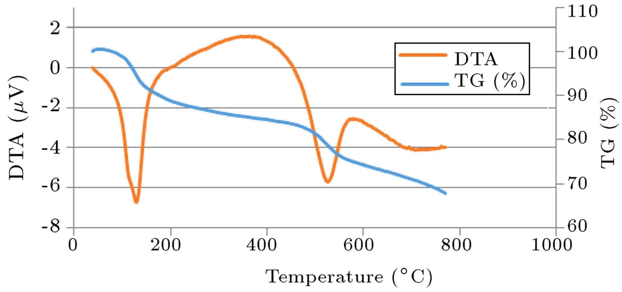


Figure 2. Thermal gravimetric analysis (TGA-DTG) pattern of nano kaolin-SO_3H.

The thermal gravimetric analysis (TGA-DTG) pattern of nano kaolin-SO_3H was detected from 20 to 780°C (Figure 2).

The catalyst was stable until 50°C, and only 4.16% of its weight was reduced at 50°C. Three endothermic processes were accumulated between 50-190°C due to the decomposition of –SO_3H group and elimination of SO_2 and H_2O from the catalyst. Between 190-330°C, its weight was nearly constant, and only 3.37% of mass was reduced. Two processes between 330-460°C and 460-510°C led to the mass changes equal to 3.77% and 14.4%, respectively, due to dehydroxylation of kaolin.

Powder X-ray diffraction studies were performed for nano kaolin-SO_3H. The obtained diffractogram is displayed in Figure 3. As shown in this figure, incorporation of –SO_3H leads to some changes in the diffractogram of kaolin nanoparticles. In the diffractogram of kaolin nanoparticles, in 2θ from 62 to 74, there were nine peaks; however, in kaolin-SO_3H nanoparticles, there were only three peaks (at 70.60, 72.67, and 74.08). In kaolin-SO_3H nanoparticles, three peaks in 2θ from 20 to 25 disappeared. Other peaks in kaolin and nano kaolin-SO_3H diffractograms were in the same position. The sharpness of peaks in the kaolin-SO_3H nanoparticles diffractogram shows the crystalline form of the catalyst.

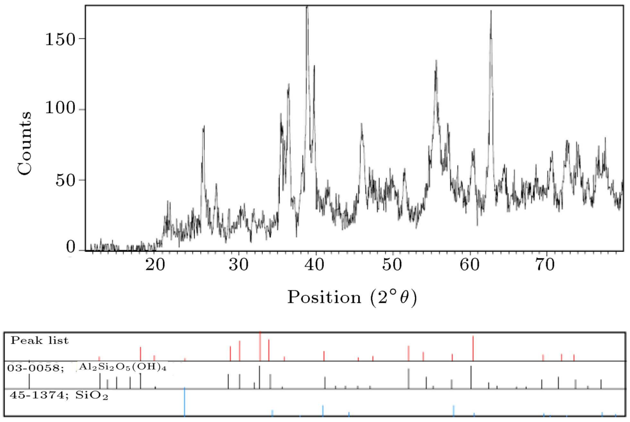


Figure 3. X-Ray Diffraction (XRD) pattern of nano kaolin-SO_3H.

Table 1. The results of X-ray fluorescence data of nano kaolin-SO_3H.

Element	**SiO_2**	**Al_2O_3**	**SO_3**	**CO_2**
Percent %	43	30.5	15.9	8.2

The Field Emission Scanning Electron Microscope (FESEM) and Transition Electron Microscope (TEM) images of the nano kaolin-SO_3H are displayed in Figure 4(a) and (b). These images clearly show the amorphous surface morphology of the nano kaolin-SO_3H with an average size distribution of 50 nm.

The X-ray fluorescence results of nano kaolin-SO_3H showed the presence of 15.9% SO_3 in its composition (Table 1).

Energy-Dispersive X-ray Spectroscopy (EDS) of nano kaolin-SO_3H was measured by EDS instrument, providing the presence of the expected elements in the structure of this catalyst and confirming supporting of SO_3H on nano-kaolin (Figure 5).

The acidity of the catalyst was compared with that of kaolin. The pH of 0.05 g of commercial kaolin or that of nano kaolin-SO_3H in 5 mL of distilled water can be 6 and 3.4, respectively. The acidic capacity of catalyst was determined via titration of 0.05 g of it with 12.16 mL of NaOH 0.009 N. The result showed 2.268 meq/g H^+.

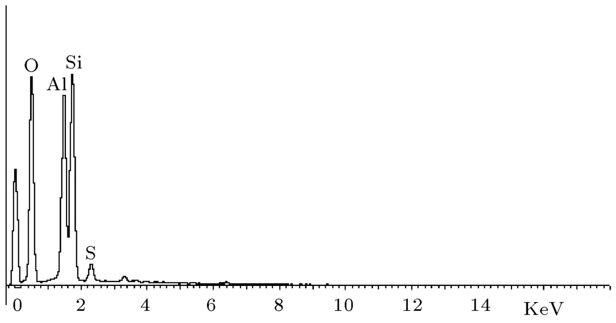


Figure 5. EDS analysis diagram of nano kaolin-SO_3H.

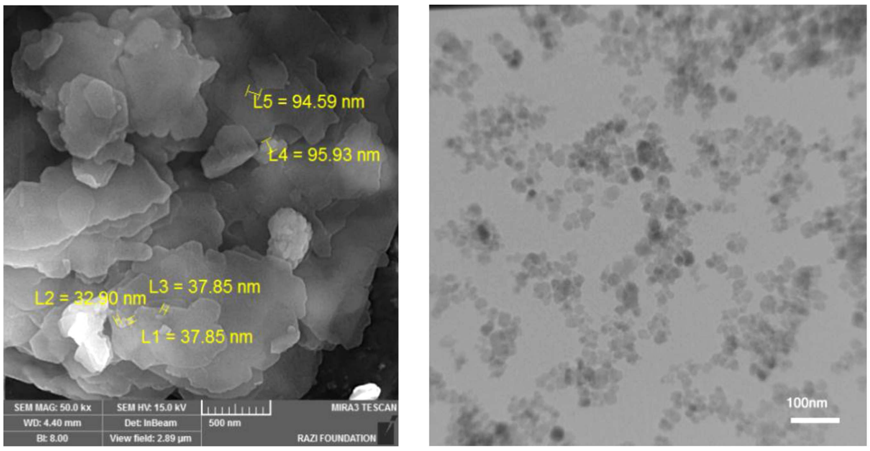
3.2. Preparation of 2,4,5-trisubstituted imidazoles in different conditions

Further to our investigations of solid acids in organic synthesis, this study reports the application of kaolin sulfonic acid nanoparticles as a new efficient heterogeneous catalyst for the synthesis of 2,4,5-trisubstituted imidazoles via reaction of benzil, 2-nitro benzaldehyde, and ammonium acetate. The reaction in different conditions is summarized in Table 2.

As shown in Table 2, nano kaolin-SO_3H is more active than catalysts listed in entries 19-26 are. The best efficiency was obtained by using 0.05 g of nano kaolin-SO_3H at 140°C in the absence of the solvent just over 7 minutes of reaction (Table 2, entry 11).

One of the outstanding advantages of kaolin sulfonic acid nanoparticles is its ability to be a recyclable reaction medium and reused for four subsequent reactions (Figure 6).

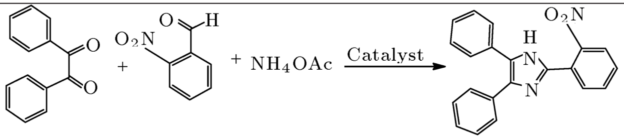
According to the optimized condition for one-pot synthesis of 2,4,5-trisubstituted imidazoles by nano



(a) (b)

Figure 4. (a) FESEM and (b) TEM photographs of nano kaolin-SO_3H.

Table 2. Synthesis of 2-(2-nitro phenyl)-4,5-diphenyl-1*H*-imidazole under various conditions.



Entry	Catalyst (g)	Solvent	Conditions	Time (min)	Yield (%)	Ref
1	Nano kaolin-SO_3H (0.01)	Solvent-free	110°C	45	42	–
2	Nano kaolin-SO_3H (0.01)	Solvent-free	120°C	45	54	–
3	Nano kaolin-SO_3H (0.01)	Solvent-free	130°C	35	60	–
4	Nano kaolin-SO_3H (0.01)	Solvent-free	140°C	30	64	–
5	Nano kaolin-SO_3H (0.01)	Solvent-free	150°C	30	63	–
6	Nano kaolin-SO_3H (0.01)	Solvent-free	160°C	30	63	–
7	Nano kaolin-SO_3H (0.02)	Solvent-free	140°C	30	72	–
8	Nano kaolin-SO_3H (0.03)	Solvent-free	140°C	25	80	–
9	Nano kaolin-SO_3H (0.035)	Solvent-free	140°C	17	84	–
10	Nano kaolin-SO_3H (0.04)	Solvent-free	140°C	12	90	–
11	Nano kaolin-SO_3H (0.05)	Solvent-free	140°C	7	95	–
12	Nano kaolin-SO_3H (0.05), 2nd run	Solvent-free	140°C	7	87	–
13	Nano kaolin-SO_3H (0.05), 3rd run	Solvent-free	140°C	7	65	–
14	Nano kaolin-SO_3H (0.05), 4th run	Solvent-free	140°C	7	43	–
15	Nano kaolin-SO_3H (0.06)	Solvent-free	140°C	9	93	–
16	Nano kaolin-SO_3H (0.07)	Solvent-free	140°C	10	94	–
17	–	Solvent-free	160°C	180	20	–
18[a]	Kaolin-SO_3H (0.05)	EtOH/H_2O (50% v/v)	80°C	90	–	–
19[b]	L-proline	Solvent-free	110°C	180	90	[12]
20[b]	[EMIM]OAc (0.017)	Ultrasound	r.t	42	87	[14]
21[b]	K10 (0.01)	EtOH	Reflux	90	85	[13]
22[b]	ZMS-5 (0.01)	EtOH	Reflux	108	84	[13]
23[b]	Sulfated zirconia, SZ (0.01)	EtOH	Reflux	96	82	[13]
24[c]	[EMIM]OAc	EtOH	Sonication	90	87	[14]
25	Nano silica phosphoric acid	–	140°C	180	88	[15]
26[b]	SBSSA[d]	–	140°C	30	95	[20]

[a] Benzil (2 mmol), terephthaldehyde (1 mmol), NH_4OAc (12 mmol).
[b] Benzil (1 mmol), benzaldehyde (1 mmol), NH_4OAc (6 mmol).
[c] Benzil (1 mmol), 4-nitrobenzaldehyde (1 mmol), NH_4OAc (10 mmol)
[d] Silica-bonded S-sulfonic acid.

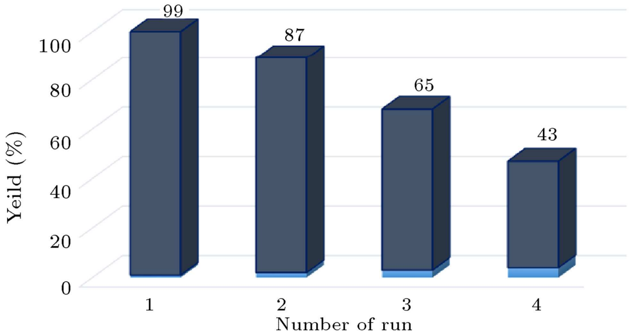


Figure 6. Reusability diagram of nano kaolin-SO_3H in one-pot synthesis of 2,4,5-trisubstituted imidazole.

kaolin-SO_3H, various products were synthesized with high purity and yields (Table 3).

3.3. Mechanisms of the synthesis of 2,4,5-trisubstituted imidazoles

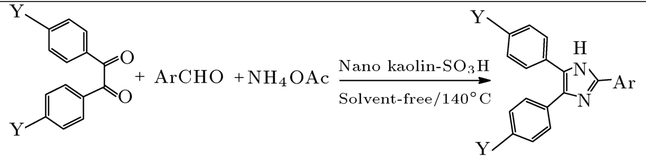
Two suggested mechanisms for the synthesis of 2,4,5-trisubstituted imidazoles are shown in Scheme 2. In path A, at first, the solid acid catalyst protonates the carbonyl group of aldehyde, which is then condensed with ammonia from ammonium acetate to produce corresponding aldimine. The second NH_3 is condensed with aldimine to form a diamine. In the presence of a catalyst, the carbonyl groups of 1,2-diketone are protonated and reacted with the diamine. By ring closure, a five-membered ring as the 2,4,5-trisubstituted imidazole is produced by the removal of water.

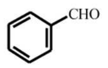
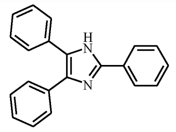
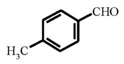
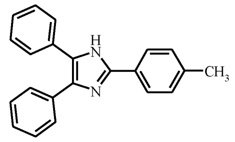
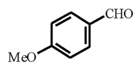
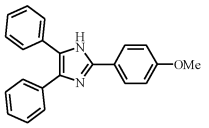
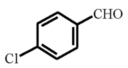
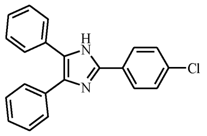
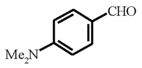
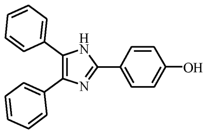
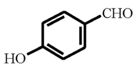
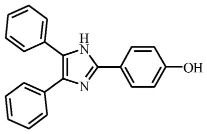
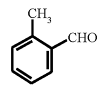
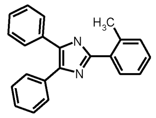
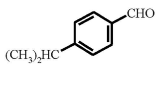
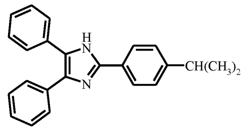
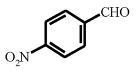
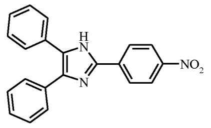
In Path B of Scheme 2, at first, the solid acid catalyst protonates the carbonyl group of aldehyde and 1,2-diketone. Then, the protonated carbonyl groups are condensed with ammonia, independently. Two intermediates react with each other. By ring closure, a five membered ring as the 2,4,5-trisubstituted imidazole is produced by the removal of water.

To explore the scope and limitations of this reaction and to establish the reaction mechanism, a study on various aspects of the process was carried out. Unique and interesting results were derived.

To study the behavior of aromatic, aliphatic, and α,β-unsaturated aldehydes in the one-pot synthesis of

Table 3. One-pot synthesis of 2,4,5-trisubstituted imidazoles in the presence of nano kaolin-SO_3H at 140°C under solvent-free conditions[a].



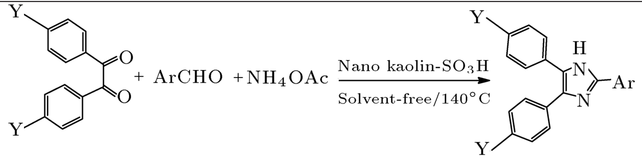
Entry	ArCHO	Y	Products	Time (min)	Yeild (%)	M.P (°C)		
						Found	Reported	Ref.
1		H		9	91	273-275	275 -276	[14]
2		H		12	87	229-231	230-233	[32]
3		H		12	89	231-233	230-231	[13]
4		H		7	84	262-264	260-262	[13]
5		H		8	84	257-259	259-262	[32]
6		H		7	81	265-267	265-267	[32]
7		H		21	71	205-207	204-206	[33]
8		H		15	89	252-253	253-255	[34]
9		H		25	78	240-242	239-242	[34]

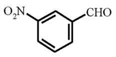
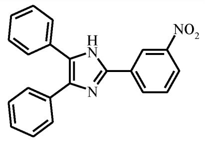
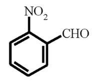
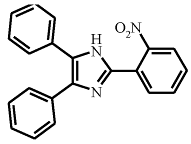
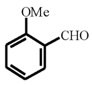
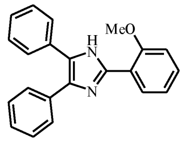
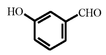
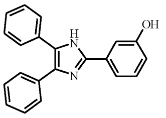
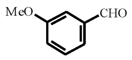
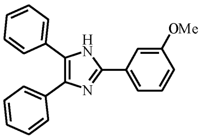
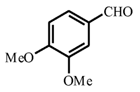
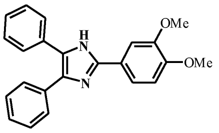
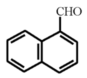
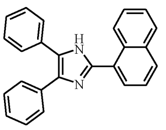
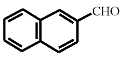
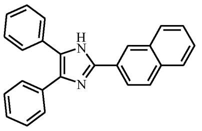
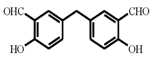
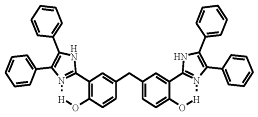
[a] Benzil (1 mmol), aldehyde (1 mmol), NH_4OAc (6 mmol), nano kaolin-SO_3H (0.05 g);

[b] Benzil (2 mmol), aldehyde (1 mmol), NH_4OAc (1 mmol), nano kaolin-SO_3H (0.10 g);

[c] 4,4′-Diflourobenzil (1 mmol), aldehyde (1 mmol), NH_4OAc (6 mmol), nano kaolin-SO_3H (0.05 g).

Table 3. One-pot synthesis of 2,4,5-trisubstituted imidazoles in the presence of nano kaolin-SO_3H at 140°C under solvent-free conditions[a] (continued).



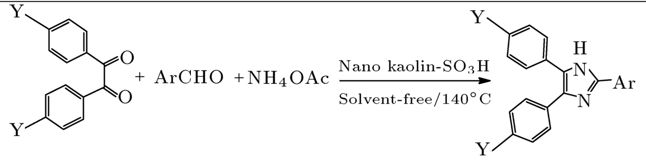
Entry	ArCHO	Y	Products	Time (min)	Yeild (%)	M.P (°C)		
						Found	Reported	Ref.
10		H		29	65	308-309	311-312	[32]
11		H		7	99	229-231	230-231	[34]
12		H		9	95	210-212	210-211	[34]
13		H		31	69	258-260	258-260	[32]
14		H		24	75	265-266	266-268	[32]
15		H		25	80	215-217	213-216	[32]
16		H		11	78	215-217	215-216	[34]
17		H		13	80	272-274	273-276	[32]
18[b]		H		35	83	244-247	-	-

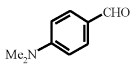
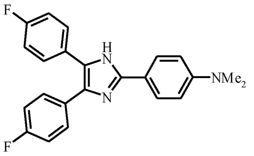
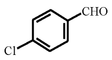
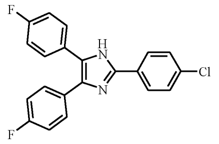
[a] Benzil (1 mmol), aldehyde (1 mmol), NH_4OAc (6 mmol), nano kaolin-SO_3H (0.05 g);

[b] Benzil (2 mmol), aldehyde (1 mmol), NH_4OAc (1 mmol), nano kaolin-SO_3H (0.10 g);

[c] 4,4′-Diflourobenzil (1 mmol), aldehyde (1 mmol), NH_4OAc (6 mmol), nano kaolin-SO_3H (0.05 g).

Table 3. One-pot synthesis of 2,4,5-trisubstituted imidazoles in the presence of nano kaolin-SO_3H at 140°C under solvent-free conditions[a] (continued).

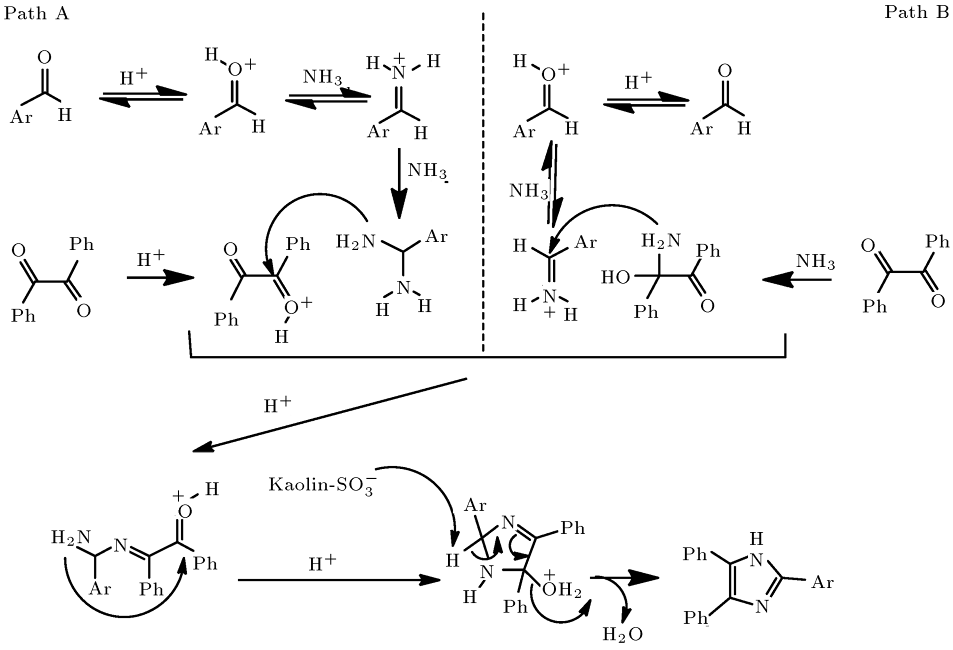


Entry	ArCHO	Y	Products	Time (min)	Yeild (%)	M.P (°C)		
						Found	Reported	Ref.
19[c]		F		33	60	269-271	–	–
20[c]		F		10	97	272-274	270-273	[32]

[a] Benzil (1 mmol), aldehyde (1 mmol), NH_4OAc (6 mmol), nano kaolin-SO_3H (0.05 g).

[b] Benzil (2 mmol), aldehyde (1 mmol), NH_4OAc (1 mmol), nano kaolin-SO_3H (0.10 g).

[c] 4,4′-diflourobenzil (1 mmol), aldehyde (1 mmol), NH_4OAc (6 mmol), nano kaolin-SO_3H (0.05 g).



Scheme 2. Two suggested mechanisms for one-pot synthesis of 2,4,5-trisubstituted imidazoles in the presence of nano kaolin-SO_3H.

2,4,5-trisubstituted imidazoles, this process was used in various aldehydes. As expected, it was observed that, unlike aromatic aldehydes which quickly led to the formation of the product, aliphatic and α,β-unsaturated aldehydes did not react. According to the mechanisms of this reaction, it is clear that mild heterogeneous catalysts are not able to protonate the carbonyl groups of the above-mentioned aldehydes.

The reactions of benzaldehyde derivatives bearing either electron-releasing or electron-withdrawing substituents in the ortho, meta, or para positions were studied. The reaction was proceeded in all cases;

however, it was very efficient in aldehydes bearing either electron-releasing or electron-withdrawing substituents in the ortho position. Aldehydes with substituents in the meta position had very low efficiency, and aldehydes with substituents in the para position were middle. According to the mechanisms of this reaction, the overall resonance and inductive effects led to such behavior. In this regard, the maximum and minimum yields were formed with ortho and meta nitro benzaldehydes, respectively.

4. Conclusion

In this paper, nano kaolin-SO_3H was prepared and characterized with FT- IR, XRD, SEM, XRF, TGA, EDS, and TEM. This study managed to introduce a new efficient and environmentally friendly pathway for one-pot synthesis of 2,4,5-trisubstituted imidazoles *via* condensation of benzil, aldehyde derivatives, and ammonium acetate using nano kaolin-SO_3H as a recyclable solid acid catalyst. This simple procedure is solvent-free; its easy and clean workup, high yields, reusability of catalyst, and heterogeneous conditions make it attractive for large-scale environment-friendly operations.

Acknowledgments

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Biographies

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