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Nano-$SbCl_5/SiO_2$ as an Efficient Catalyst for One-Pot Synthesis of 2, 4, 5-Trisubstituted Imidazoles Under Solvent-Free Condition

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Abstract

A general synthetic route to the synthesis of imidazoles has been developed using nano $SbCl_5/SiO_2$ under solvent-free conditions. The multi-component reactions of aldehydes, benzil and ammonium acetate were carried out to afford some trisubstituted imidazole derivatives. This method provides several advantages like simple work-up, environmentally benign, and shorter reaction times along with high yields. The mentioned nano catalyst was investigated by SEM, TEM and XRD. Meanwhile, structures of trisubstituted imidazoles were elucidated by FT-IR, ^{1}H NMR and ^{13}C NMR spectra.

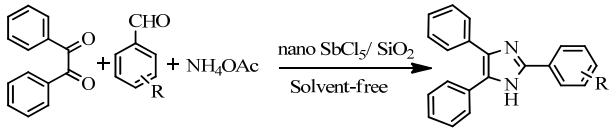
1. Introduction

Over the past decades, multicomponent reactions (MCRs) have proved to be very powerful and efficient bond-forming tools in organic, combinatorial and medicinal chemistry in the context of green chemistry [1-4]. The MCRs are very flexible, atom economic in nature, and proceed through a sequence of reaction equilibrium, yielding the target product [5-8]. Along with other reaction parameters, the nature of the catalyst plays a significant role in determining yield, selectivity, and general

applicability [9, 10]. Thus, development of an inexpensive, mild, reusable, and general catalyst for MCRs remains an issue of interest. The chemical synthesis productivity can be enhanced by nano sized catalysts because of their extremely low size and their high surface to volume ratios. Moreover, to improve catalyst separation much try has been devoted to chemical reactions at heterogeneous mode [11-13]. On the other hand imidazole derivatives are a very interesting class of heterocyclic compounds because they have many pharmacological properties and play important roles in biochemical processes [14].

As a part of our continued interest in catalysis by solid acids or nanoparticles [15-24], we found excellent reactivity of nano $SbCl_5/SiO_2$ for a MCR in high yields. Some advantages of using nano $SbCl_5/SiO_2$ are ease to synthesize at room temperature from readily available and inexpensive materials, stability at elevated temperatures, neutrality, and biocompatibility [25-27]. Besides the above mentioned characteristics, higher reactivity and excellent selectivity of the nano $SbCl_5/SiO_2$ prompted us to explore its full potential in other MCRs leading to products with practically important biological, pharmacological, and optical properties.

In this paper, we report nano $SbCl_5/SiO_2$ catalyzed synthesis of imidazole derivatives via a one-pot three component condensation of aldehydes, benzil and ammonium acetate in solvent-free conditions.



Scheme1. Synthesis of 2, 4, 5- trisubstituted imidazoles using nano $SbCl_5/SiO_2$ under solvent-free conditions

2. Experimental

2.1 Materials and characterization

All reagents were purchased from Merck and Aldrich and used without further purification. The products were isolated and characterized by physical and spectral data. ^1H NMR and ^{13}C NMR spectra were recordedon Bruker (DRX Avance-400) spectrometers in the presence of tetramethylsilane as internal standard. The IR spectra were recorded on FT-IR Magna 550 apparatus using with KBr plates. Melting points were determined on Electro thermal 9200, and are not corrected. Powder X-ray diffraction (XRD) was carried out on a Philips diffractmeter of X'pert MPD Company with mono chromatized Cu Kα radiation (λ=1.5406 Å). Microscopic morphology of products was visualized by SEM (VEGA/TESCAN) scanning electron microscope.

2.2. Synthesis of nano $SbCl_5.SiO_2$

The catalyst was prepared by stirring a mixture of $SbCl_5$ (0.7 ml) and nano silica gel (20 nm, 1 g) in 5 ml of chloroform for 1 h at room temperature. The slurry was filtered and washed with chloroform. The obtained solid (62% nano $SbCl_5.SiO_2$) was dried at ambient temperature for 2 h and then stored in a dry container [28]. The XRD pattern of the pure SiO_2 nanoparticles is shown in Figure 1. All reflection peaks can be readily indexed to pure cubic crystal phase of nano silica gel. Also XRD of the nano $SbCl_5/SiO_2$ is shown in Figure 2. As it shows peaks for pure SiO_2 and $SbCl_5$ exist in this pattern that proof antimony pentachloride is supported on nano silica gel.

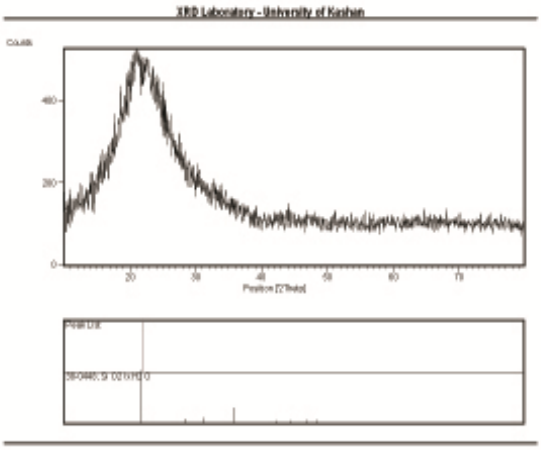


Fig. 1. The XRD pattern of nano SiO_2

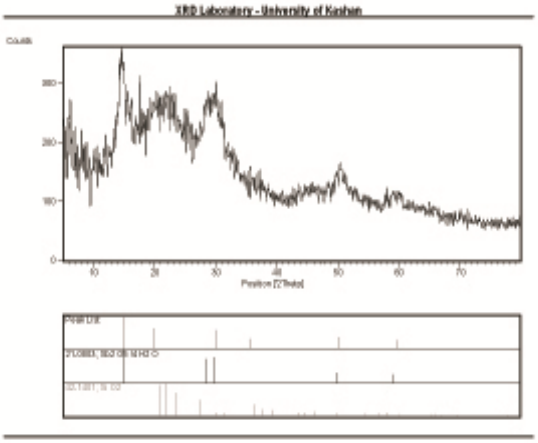


Fig. 2. The XRD pattern of nano $SbCl_5/SiO_2$

To obtain a visual image of the nano-$SbCl_5/SiO_2$, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out. By SEM and TEM images some information about the morphology of the catalyst particles was obtained as presented in Figure 3. As can be seen from the figure, the sample shows a nano crystalline structure.

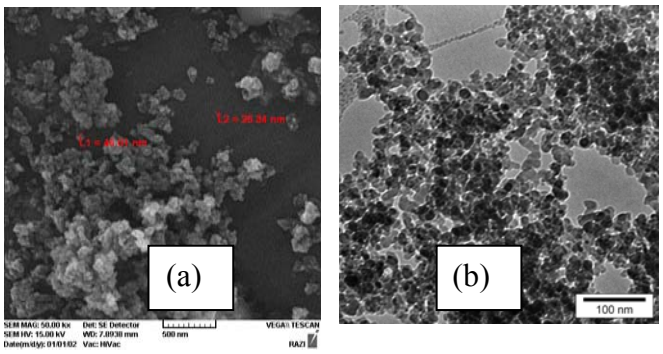


Fig. 3. a)SEM and b) TEM image of nano-$SbCl_5/SiO_2$

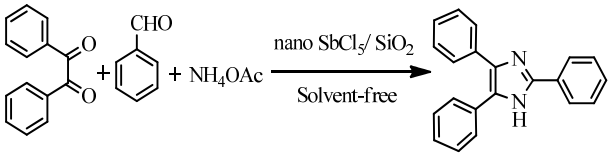
2.3. General procedure for the preparation of 2, 4, 5-tri substituted imidazole derivatives

A mixture of benzil (1 mmol), aldehyde (1 mmol), and ammonium acetate (3 mmol), nano $SbCl_5/SiO_2$ (0.05 g) was finely grinded and heated with stirring at 115 $^{\circ}$C in an oil bath. The reaction was monitored by TLC. After cooling, dichloromethane was added to the mixture and filtered to remove the catalyst. Dichloromethane was evaporated and the crude product crystallized from ethanol to afford the pure product. All of the products were characterized and identified with melting point, ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy techniques.

3. Results and discussion

Herein we wish to report a simple and convenient method for the synthesis of 2, 4, 5-tri substituted imidazoles by condensation of aldehydes with benzil and ammonium acetate under solvent-free conditions in the presence of nano $SbCl_5/SiO_2$ as catalyst (Scheme 1). Nano $SbCl_5/SiO_2$ is an inexpensive heterogeneous reagent, which can be prepared easily. Safety and ease in handling, rate enhancement, high yields and easy work up procedures are the properties which made us to use this interesting reagent as a catalyst. To the best of our knowledge there are no

reports on the applicability of nano $SbCl_5/SiO_2$ for the synthesis of 2, 4, 5-tri substituted imidazoles in the literature.



Scheme 2. The model reaction for the synthesis of 2, 4, 5-tri substituted imidazoles in the presence of nano-$SbCl_5/SiO_2$

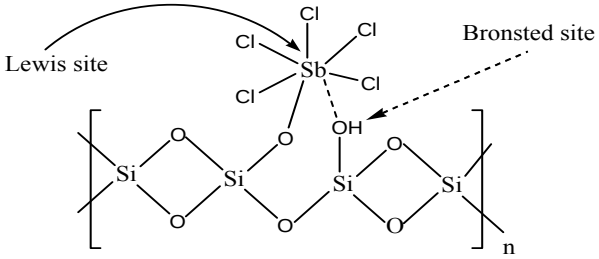
In the preliminary experiments the catalytic behaviors of some types of catalyst were compared in the reaction of benzaldehyde, benzil and ammonium acetate in solvent-free conditions (Table1). In absence of catalyst, the reaction did not progress at all. Notably, antimony penta chloride supported nano silica gel shows an activity higher than those of reported heterogeneous, we believe that nano silica gel surface chemistry plays an important role in this reaction.

Table 1. Optimization of the model reaction using various catalysts

Entry	Catalyst[a]	Time (min)	Yiled, (%)[b]
1	None	150	trace
2	$SbCl_5$	110	25
3	Nano-SiO_2	110	15
4	$SbCl_5.SiO_2$	80	75
5	nano $SbCl_5/SiO_2$	20	96

[a]The reaction was carried out under solvent-free conditions.
[b]Isolated yield.

To determine the optimum quantity of nano silica supported antimony pentachloride in reaction of benzaldehayde, benzil and ammonium acetate under solvent free conditions, we used different amounts of nano $SbCl_5/SiO_2$. The best amount of corresponding catalyst was obtained 0.05 g. The study was then extended to the application of nano $SbCl_5/SiO_2$ in synthesis of trisubstituted imidazoles of various aldehydes with benzil and ammonium acetate. The best result was obtained in model reaction at solvent free conditions and at the presence of nano $SbCl_5/SiO_2$ 0.05 g. The results are listed in Table 2. Nano $SbCl_5/SiO_2$ can act as Bronsted and Lewis acid (empty π orbital of Sb in nano $SbCl_5/SiO_2$) catalysts [29], as illustrated in Scheme 3.



Scheme 3. Bronsted acidity arising from inductive effect of Lewis acid center coordinated to nano silica gel

Table 2. Preparation of 2, 4, 5-trisubstituted imidazole derivatives by using nano $SbCl_5/SiO_2$ as catalyst (Scheme 1)

Product	R	Time (min)	Yield[a] %	M.p (^oC)
1	H	20	96	273-274
2	4-OMe	22	95	227-228
3	4-Me	20	78	163-164
4	4-NO_2	33	86	232-233
5	4-Cl	22	95	262-263
6	2,3-Cl_2	30	91	173-174
7	4-^{i}pr	28	92	230-231
8	4-$N(CH_3)_2$	25	90	255-256
9	3,4-OMe_2	32	90	158-159
10	3-NO_2	30	89	240-241

[a]Yields refer to the pure isolated products.

4. Conclusion

To sum up, we have reported that nano $SbCl_5/SiO_2$ are a highly efficient catalyst for the synthesis of 2, 4, 5-trisubstituted imidazoles by means of a multi-component condensation of an aldehydes, benzil and ammonium acetate in one pot. This method is applicable to a wide range of substrates, including aromatic aldehydes, and provides the corresponding imidazoles in good to excellent yields. The present methodology offers advantages such as reduced reaction times, high yields, operational simplicity, reduced toxicity of nano $SbCl_5/SiO_2$, along with heterogeneous catalyst.

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