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Nano-sawdust-$SbCl_5$ as a new, green and effective nano catalyst for one-pot synthesis of pyrano [4,3-*b*] pyrans

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Nano-sawdust-$SbCl_5$ as a new and mild solid acid catalyst is applied to the synthesis of biologically important pyrano [4,3-*b*] pyrans. The reaction involves the use of 4-hydroxy-6-methyl-2*H*-pyran-2-one, malononitrile and aldehydes. The procedure is very simple and the products are isolated with an easy workup in good-to-excellent yields. The morphology of nanocatalyst (nano-sawdust-$SbCl_5$) was observed using a scanning electron microscopy (SEM). Also, the vibrational spectrum analysis (FT-IR) of the catalyst has been performed.

Keywords: Nano-sawdust-$SbCl_5$, Pyranopyrans, Multicomponent Reaction, Malononitrile, Green chemistry

INTRODUCTION

Multi-component reactions, by virtue of their convergence are widely applied in pharmaceutical chemistry in order to producing different structures and combinatorial libraries for drug discovery [1]. Pyrano [4,3-*b*] pyrans are some examples of multi-component reactions. Recently, the syntheses of pyran derivatives are attractive because they generally show biological properties such as insecticidal, antiviral, antileishmanial and antimicrobial activities [2-5].

Despite their importance, comparatively few methods for accessing pyrano [4,3-*b*] pyrans derivatives have been reported [6-12].

Nowadays in order to design green experimental protocols for the synthesis of organic compounds, chemists are trying to explore alternative reaction conditions and reaction media to accomplish the desired chemical transformations and minimize the by-products or wastes. So by using solvent free reactions, microwave and ultrasonic irradiations can help us achieve the aforementioned goal [13-17].

In addition, heterogeneous solid acids have advantages such as simplicity in handling, economic regulations, easy recovery and frequent use without loss of their efficiency over in comparison with conventional homogeneous acid catalysts.

The sawdust consists of cellulose, lignin and hemicelluloses that cellulose is composed of a long chain of glucose molecules, lignin is a complex polymer composed of phenylpropane units, and hemicelluloses are branched polymers composed of xylose, arabinose, galactose, mannose, and glucose [18-21]. The lignocellulosic material of sawdust includes a wide variety of hydroxyl groups that can be used as active sites for the preparation of solid acid catalysts.

In this study, the sawdust has been used as an adsorbent for the preparation of nano-sawdust-$SbCl_5$ which has average small size and is well distributed.

In continuation of our previous research on the use of nano solid acids in organic synthesis [22-29], nano-sawdust-$SbCl_5$, as a new nano catalyst, has been applied for the synthesis of pyrano [4,3-*b*] pyrans derivatives.

EXPERIMENTAL

All chemicals were purchased from Fluka or Merck Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Melting points were recorded on an Electrothermal 9100 apparatus in open capillary tubes. IR spectra were recorded on a Shimadzu IR-470 spectrometer. The ^{1}H NMR spectra were recorded on Bruker DRX-400 Avance spectrometer at solution in DMSO-d_6 using TMS as the internal standard. The IR spectrum of the catalyst was recorded using a model Bruker Tensor 27 FT-IR operating within the range of 400-4000 cm^{-1}. The morphologies of the nanoparticles were observed using FESEM of a MIRA3 TESCAN microscope with an accelerating voltage of 15 kV.

Synthesis of nano-sawdust-$SbCl_5$

The sawdust was collected from sawmill in Farrokhi city, Iran. Sawdust was washed several times to remove adhering dirt and then dried at 60 °C for 24 h. The dried sawdust was ground to pass through a 1 mm sieve and labeled as sawdust [27]. The reagent was prepared by stirring a mixture of $SbCl_5$ (0.7 ml) and 1 g of sawdust powder in 5 ml of chloroform for 1 h at room temperature. The slurry was filtered and washed with chloroform. The obtained solid (nano-sawdust-$SbCl_5$) was dried in an

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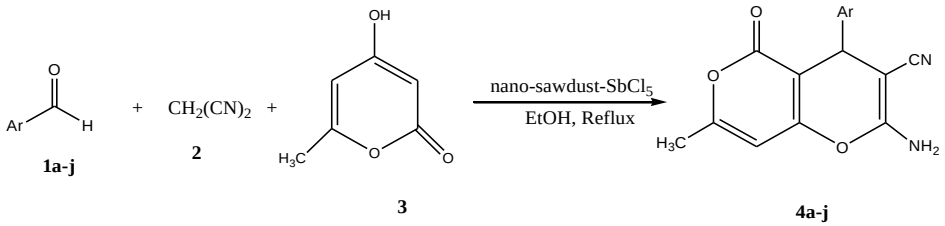
oven at 60°C for 4h and then pulverized at the mortar. The size of particles was obtained below 50 nm using SEM.

General procedure for the preparation of compounds 4a-j

A mixture of aromatic aldehyde (1 mmol), malononitrile (1.2 mmol) and 4-Hydroxy-6-methyl-2*H*-pyran-2-one (1 mmol) in 5 mL of EtOH was refluxed for the appropriate time in the presence of nano-sawdust-$SbCl_5$ (0.006g). After completion of reaction, as indicated by TLC (*n*-hexane:ethyl acetate 3:1), the reaction mixture was filtered to remove the catalyst. After evaporation of the solvent, the crude product was re-crystallized from hot ethanol to obtain the pure compound.

RESULTS AND DISCUSSION

In continuation of our investigation into the application of solid acids in organic synthesis, we studied the application of sawdust as a green, inexpensive and available surface to synthesis of solid acid nano catalyst. In this study, nano-sawdust-$SbCl_5$ was prepared and described. The catalytic activity of nanoparticles was investigated for synthesis of pyrano [4,3-*b*] pyran derivatives, by the condensation of an aldehyde **1a-j**, malononitrile **2** and 4-Hydroxy-6-methyl-2*H*-pyran-2-one **3** (Scheme 1).



Scheme 1. Synthesis of pyrano [4,3-*b*] pyran derivatives in the presence of nano-sawdust-$SbCl_5$ as catalyst

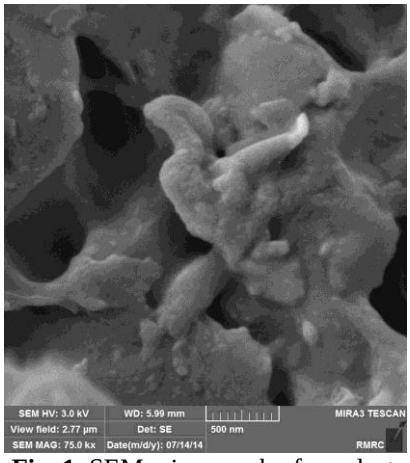


Fig. 1. SEM micrograph of sawdust

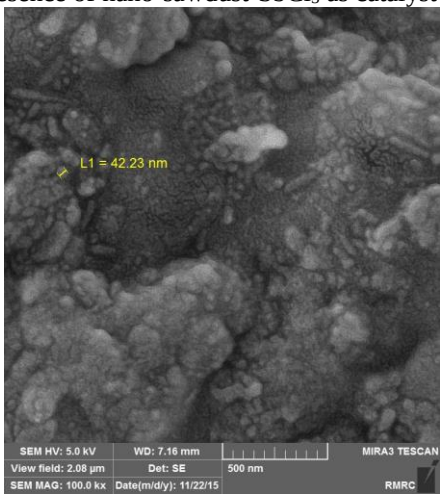


Fig. 2. SEM micrograph of nano-sawdust-$SbCl_5$

The morphology and size of sawdust (Fig. 1) and nano-sawdust-$SbCl_5$ was observed by SEM images. As shown in Figure 2, the size of nano-sawdust-$SbCl_5$ is below 50 nm and homogeneous nano sheet surface was revealed.

In FT-IR spectrum of nano-sawdust-$SbCl_5$ catalyst (Fig. 3), showed the hydroxyl bonds of sawdust catalysis at 3566 cm^{-1}. The peak at 1616 cm^{-1} is assigned to C=C stretching vibrations of present in phenyl rings of lignin unit. In the FT-IR spectrum of sawdust-$SbCl_5$, the C-O and Sb-O were observed in the 1155 cm^{-1} and 592 cm^{-1}, respectively. The FT-IR data's approved the actual event of chemical interaction of antimony pentachloride with the surface area of sawdust.

In order to determine the optimum quantity of nano-sawdust-$SbCl_5$, the reaction of 4-Hydroxy-6-methyl-2*H*-pyran-2-one, malononitrile and benzaldehyde was carried out under reflux in ethanol using different quantities of nano-sawdust-$SbCl_5$. As shown in Table 1, 0.006g of nano-sawdust-$SbCl_5$ gives an excellent yield in 15 min.

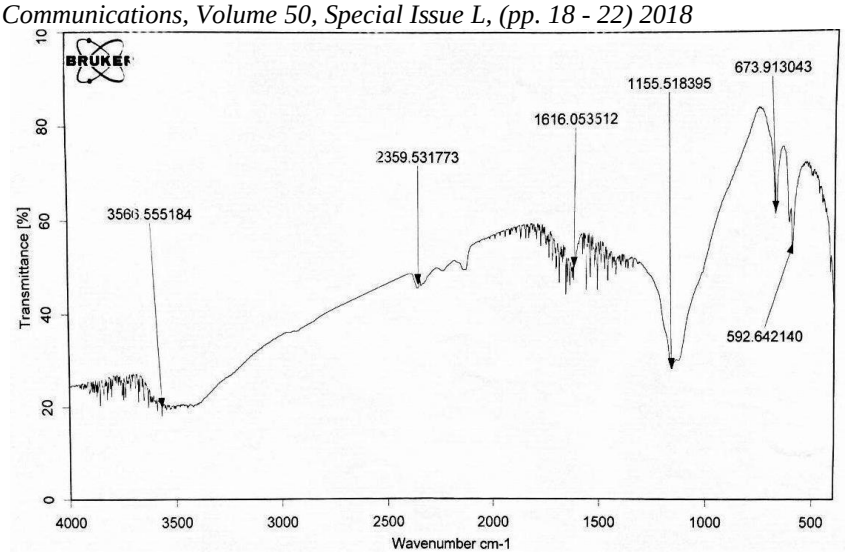


Fig. 3. FT IR spectrum of nano-sawdust-$SbCl_5$ catalyst.

Table 1. Optimization of the reaction conditions for synthesis of 4a

Entry	Catalyst (amount)	Solvent/Condition	Time(min)	Yield
1	Nano-sawdust-$SbCl_5$ (0.006 g)	CH_2Cl_2/Reflux	15	34
2	Nano-sawdust-$SbCl_5$ (0.006 g)	EtOH/Reflux	15	94
3	Nano-sawdust-$SbCl_5$ (0.006 g)	CH_3CN/Reflux	15	46
4	Nano-sawdust-$SbCl_5$ (0.006 g)	MeOH/Reflux	15	59
5	Nano-sawdust-$SbCl_5$ (0.006 g)	H_2O/Reflux	15	85
6	Nano-sawdust-$SbCl_5$ (0.004 g)	EtOH/Reflux	15	69
7	Nano-sawdust-$SbCl_5$ (0.008 g)	EtOH/Reflux	15	95
8	Nano-sawdust-$SbCl_5$ (0.006 g) 2nd run	EtOH/Reflux	15	90
9	Nano-sawdust-$SbCl_5$ (0.006 g) 3rd run	EtOH/Reflux	15	86
10	sawdust (0.01 g)	EtOH/Reflux	20	Trace

To study the scope of the reaction, a series of aldehydes with 4-Hydroxy-6-methyl-2*H*-pyran-2-one and malononitrile were examined by nano-sawdust-$SbCl_5$ as catalyst. The results are shown in Table 2. In all cases, aromatic aldehyde substituted with either electron-donating or electron-withdrawing groups underwent the reaction smoothly and formed products in approving yields.

Table 2. Synthesis of pyrano [4,3-*b*] pyrans [a]

Entry	Ar	Product[b]	Time(min)	Yield[c]	M.P.(˚C) [Ref.]
1	C_6H_5	4a	15	94	224-226(221-223) [30]
2	4-ClC_6H_4	4b	15	92	230-232(228-230) [31]
3	4-$CH_3OC_6H_4$	4c	15	86	200-202(200-201) [30]
4	2,4-ClC_6H_3	4d	15	87	230-232(232-235) [32]
5	3-$NO_2C_6H_4$	4e	10	92	234-236(232-233) [32]
6	4-$NO_2C_6H_4$	4f	10	90	210-212(210-212) [30]
7	4-BrC_6H_4	4g	15	89	228-230(226-227) [31]
8	2-Furanyl	4h	20	90	222-224(223-224) [31]
9	2-Thienyl	4i	20	88	245-248(242-244) [31]
10	3-indolyl	4j	20	80	209-212(206-208) [31]

[a]Ratio of aldehyde (mmol): 4-Hydroxy-6-methyl-2*H*-pyran-2-one (mmol): malononitrile (mmol): catalyst (g) is 1:1:1.2: 0.006. [b]All products are known and were identified by their melting points, IR and ^{1}H NMR spectra. [c]Isolated yield

With the above-mentioned results in hand, a plausible mechanism of this reaction was proposed in Scheme 2. The initiation step of this chain process was begun with the interaction of aldehyde **1** and nano-sawdust-$SbCl_5$ as a solid acid catalyst. The subsequent step was Knoevenagel condensation between the activated aldehyde and malononitrile **2** to form intermediate **5**. Then the Michael addition of 4-Hydroxy-6-methyl-2*H*-pyran-2-one **3** to intermediate **5** would furnish intermediate **6**. Finally, the product **4** was obtained by an intramolecular cyclization and tautomerism

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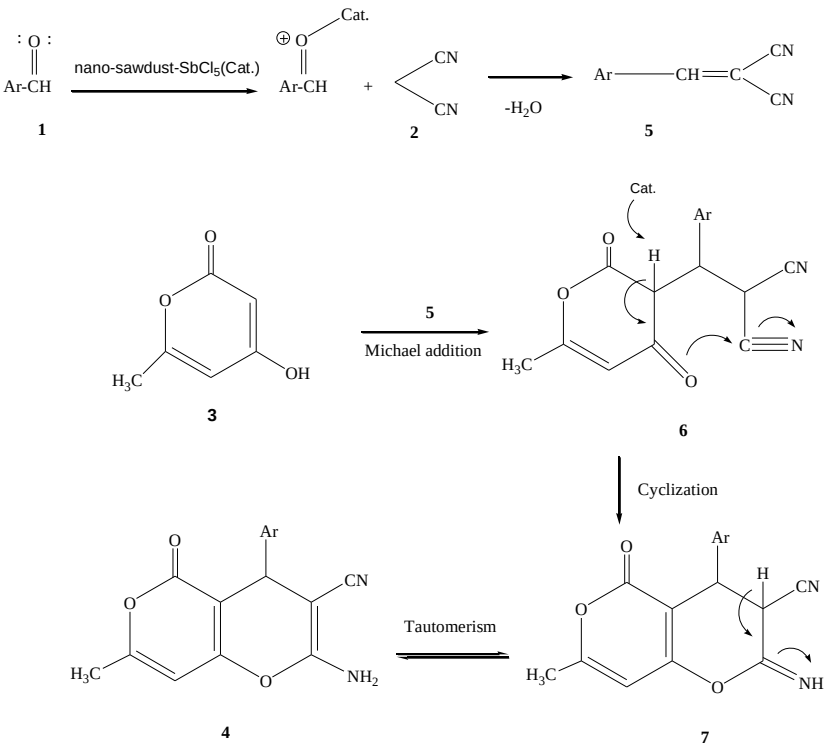

Scheme 2. Plausible mechanism for the formation of pyrano [4,3-*b*] pyran derivatives

In order to establish better catalytic activity of nano-sawdust-$SbCl_5$, the synthesis of pyrano [4,3-*b*] pyran derivatives was compared with other catalysts reported in literature [29-37]. As shown in Table 3, synthesis of these compounds catalyzed by nano-sawdust-$SbCl_5$ in EtOH offers production of the corresponding products in shorter time, much efficient yield and milder condition is done, while other methods require more amount of catalyst and longer reaction time for synthesis of pyrano [4,3-*b*] pyrans

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Table 3. Comparison of nano-sawdust-$SbCl_5$ and various catalysts in the synthesis of 4a

Entry	Catalyst	Conditions	Time	Yield	Ref.
1	Nano-cellulose-OSO_3H (0.008 g)	EtOH, Reflux	10 min	94	[29]
2	DBU (10mol %)	H_2O, Reflux	12 min	88	[30]
3	NH_4OAC (10mol %)	Solvent-free, r.t.	10 min	94	[31]
4	$KAl(SO_4)_2.12H_2O$ (10mol %)	H_2O, 80°C	1.h	76	[32]
5	Piperidine (1-2 drops)	MeOH, Reflux	1 h	79	[33]
6	TMGT (1mol %)	100 °C	1 h	77	[34]
7	-	H_2O, 80°C	10.5 h	65	[35]
8	MgO	H_2O/EtOH, Reflux	30 min	89	[36]
9	$H_6P_2W_{18}O_{62}.18H_2O$ (1mol %)	H_2O, Reflux	1 h	94	[37]
10	Nano-sawdust-$SbCl_5$ (0.006 g)	EtOH, Reflux	15 min	94	This work

CONCLUSION

The present investigation shows that nano-sawdust-$SbCl_5$ a capable nanocatalyst to be used for pyrano [4,3-*b*] pyran synthesis via one-pot reaction of aldehydes, malononitrile and 4-Hydroxy-6-methyl-2*H*-pyran-2-one. Nano-sawdust-$SbCl_5$ was successfully prepared and characterized using FTIR and SEM. Prominent among the advantages of this method are such as shorter reaction times, simple work-up, affords excellent yield, and re-usable for a number of times without appreciable loss of activity. The present method does not involve any hazardous organic solvent. Therefore, this procedure could be classified as green chemistry.

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