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Graphical Abstract

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modified nanoclay

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The NH₂-MMT as a green nanocatalyst was used for the C–N bond formation in the synthesis of azines and 2-aminothiazoles in accordance with the principles of green chemistry.



Highlights

- NH₂-MMT nanoclayas an excellent catalytic system in organic reaction.
- Introducing NH₂-MMT for the synthesis of azine and 2-aminothiazole derivatives.
- Transition-metal-free C–N bond formation at room temperature.
- The method conforms to several of the guiding principles of green chemistry.

C-N bond formation in alicyclic and heterocyclic compounds by amine-

modified nanoclay

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Abstract

In the current protocol, amine functionalized montmorillonite K10 nanoclay (NH₂-MMT) was applied to catalyze the formation of C–N bonds in the synthesis of azines and 2-aminothiazoles at room temperature. In comparison with the current methods of C–N bond formation, this approach displays specific advantages include atom economy, clean conversion, design for energy efficiency, the use of nontoxic and heterogeneous catalyst, higher purity and yields, safer solvent and reagents for this organic transformation.

Keywords: Montmorillonite, Clay, Azines, C-N bonds, 2-aminothiazole.

1. Introduction

The developments of carbon-heteroatom bonds formation reactions, especially C–N bonds, are extremely important in the chemical sciences because of their abundance in various biologically active natural products and medicinally important compounds [1]. Alicyclic azines and 2-aminothiazole heterocycles with the C–N bonds in their structure have attracted great attention for various chemical and biological applications [1.2].

Azine derivatives have been suggested for several pharmacological applications [3] and extensively used in polymerization [4], bond formation reaction [5], in the generation of

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conducting materials [6], in the design of liquid crystal [7] and the synthesis of heterocyclic systems [8]. Although, azines are well-known organic compound ever since 19th century but only a limited number of synthetic approaches is applied for their preparation [9-12]. Some of the synthetic methods suffer from disadvantages such as low yields of products, large amounts of catalyst, a large excess of one of the reagents, byproduct formation, high temperatures, long reaction time, several hours reactions, and difficult operating conditions.

On the other hands, 2-aminothiazole and its derivatives, as a significant class of heterocycles possessing a C–N bond, have attracted wide attention in medicinal chemistry due to their broad spectrums of pharmacological and biological activities. Therefore, in recent times, many efforts have been made for the preparation of this class of heterocycles [13-15]. Although these methods reported by others find certain merits of their own, some of these protocols have specific drawbacks, including high reaction temperatures, the use of expensive or toxic catalysts, reagents in stoichiometric amounts, harsh reaction conditions, tedious workup, low yields and high catalytic loading [15,16].

However, to overcome the above mentioned problem and the development of a greener and milder approach for the preparation of azines and 2-aminothiazoles, we decided to design a new process for the C–N bond formation in alicyclic and heterocyclic compounds in the presence of the heterogeneous acid–base combination catalytic system.

The use of montmorillonite-K10 (MMT-K10) has received considerable attention as catalyst or catalyst support in organic transformations due to its high chemical and thermal stability [17]. MMT as layered alumina silicate is clay that consists of two tetrahedral silicate layers with a central alumina or magnesia octahedral sheet. The organo-modified MMT widely used in the catalytic systems because of its ability to reusability, its high surface reactivity, its cheap and

nonhazardous, and its high surface area [18-20]. In this regard, several studies have been reported using immobilized amine-modified MMT (NH₂-MMT) as catalysts for many organic reactions such as Ullmann reaction [21], Henry reaction [22], Knoevenagel condensation [23], C–S coupling reactions [24], the synthesis of organic heterocycles [25], and carbonylative Sonogashira reaction [26].

There for, in this investigation, we report NH_2 -MMT as an easily separable, eco-friendly and highly effective catalyst with acid–base properties for the synthesis of azines and 2-aminothiazoles in excellent yield under mild condition (scheme 1 and 2).



Scheme 1. Synthesis of azines using NH₂-MMT.



Scheme 2. Synthesis of 2-aminothiazole using NH₂-MMT.

2. Experimental

2.1. Chemicals and apparatus

All chemicals were purchased from the Merck, Aldrich and Sigma Chemical Companies. Melting points were determined on an Electrothermal MK3 apparatus using an open-glass capillary and are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded with a Bruker DRX-

400 spectrometer at 400 and 100 MHz respectively. FT-IR spectra were obtained with KBr pellets in the range 400-4000 cm⁻¹ with a Perkin-Elmer 550 spectrometer. Nanostructures were characterized using a Holland Philips Xpert X-ray diffraction (XRD) diffractometer (CuK, radiation, λ = 0.154056 nm), at a scanning speed of 2°/min from 10° to 100° (2 θ). The surface morphology of chitosan based material was analyzed by field emission scanning electron microscopy (SEM) (EVO LS 10, Zeiss, Carl Zeiss, Germany).

2.2. Synthesis of NH₂-MMT nanoclay

The process for the amino-modification of MMT was performed in the following manner. 0.5 g MMT was added to a 15 ml solution of 3-aminopropyltrimethoxysilane (APTMS) (1.2 mmol) using n-hexane, and the suspension was stirred at room temperature for 2 h. Next, the prepared NH₂-MMT were filtered and washed three times with ethanol and n-hexane followed by drying under vacuum at temperature of 50 °C [18].

2.3. General procedure for the synthesis of azines

In a solvent-free grinding procedure, a mixture of the ketone or aldehyde (1 mmol), hydrazine sulfate (0.5 mmol), and NH₂-MMT nanocatalyst (0.2 g) was thoroughly mixed in a mortar at room temperature till the completion of catalytic process as indicated by TLC (ethyl acetate/petroleum ether 3:7) for 1-8 min. Then, ethyl acetate was added to the resultant material and the heterogeneous NH₂-MMT was separated by filtration. The solvent was evaporated under reduced pressure, and solid product was washed with water to remove any unreacted hydrazine sulfate. The product was purified by recrystallization from ethanol.

2.4. General procedure for the synthesis of 2-aminothiazoles

A mixture of methylcarbonyl (2 mmol), thiourea (3 mmol), NIS (2 mmol), and NH₂-MMT (0.10 g) in EtOH (5 mL) at room temperature was stirred until completion of reaction. The progress of the reaction was monitored by TLC (petroleum ether–ethyl acetate 4:1). After completion of the reaction, the NH₂-MMT was separated by filtration. After evaporation of EtOH under vacuum, the crude product was dissolved in boiling water and adjusted to pH=8 with the amount of ammonia to give the solid products. The solid obtained was recrystallized from a mixture of ethanol-water.

3. Results and discussion

3.1. Characterization of catalyst

The grafting of MMT with organic moieties containing amine was performed with APTES *via* silanization procedure (scheme 3) and was characterized by X-ray diffraction (XRD), energy-dispersive analysis of X-ray (EDAX), scanning electron microscopy (SEM), and fourier transform infrared spectroscopy (FT-IR). NH₂-MMT has been used as nanocatalyst for the synthesis of symmetrical azine derivatives.



Scheme 3: Preparation of NH₂-MMT nanocatalyst.

SEM images of MMT and NH₂-MMT are shown in Fig. 1. The neat MMT possesses a layered morphology consisting of broken plates. It is clear that layered structure of MMT after modification is similar to that of the parent nanoclay.



Fig. 1. SEM images of (a) and (b) MMT nanoclay; (c) and (d) NH₂-MMT.

The EDAX of the NH_2 -MMT are shown in Fig. 2. It can be obviously seen that the NH_2 -MMT contained main elements O (54.50 W%), Si (30.77 W%), Al (6.41 W%), and N (4.96 W%). These results indicate that organosilane was successfully grafted on the MMT.



Fig. 2. The EDAS spectrum of NH₂-MMT.

In Fig. 3, the XRD pattern of unmodified MMT and NH₂-MMT showed that the diffraction peaks of MMT were observed at $2\theta = 12.25$, 20.94, 35.06, and 61.89 which are assigned to the diffractions of the (002), (110, 220), (200, 130), and (060, 330) reflections, respectively [18] Furthermore, the similarity in the XRD pattern of the two samples suggests the clay structure in the MMT matrix is retained after modification.



Fig. 3. XRD patterns of (a) MMT and (b) NH₂-MMT.

The TGA results of the nanoclays are presented in Fig. 4. As can be seen, the thermogram of NH_2 -MMT exhibit significant weight loss at the temperature ranges 50–200 and 200–750 °C. The weight loss below 200 °C is usually interpreted as the loss of adsorbed water. The other losses of weight between 200 and 750 °C (about 12%) are corresponding to the thermal decomposition of organic components in nanoclay [18].



Fig. 4. TGA curves of pure MMT and silane functionalized NH₂-MMT

Fig. 5 shows the FT-IR spectrum of aminated nanoclay. The absorbance bands at 3627 and 1043 cm⁻¹ are related to Al–O–H and O–Si stretching vibration, respectively. The absorption peak at 3434 cm⁻¹ correspond to the NH₂ groups stretching mode and a weak peak at 2928 cm⁻¹ is attributed to the –CH stretching vibration. Moreover, the absorption peaks at 571 and 468 cm⁻¹ is assigned for the Al-O and Mg-O stretching vibration respectively [18].



Fig. 5. FT-IR spectra of (a) MMT and (b) NH₂-MMT.

2.3. Catalytic performance of NH₂-MMT in the synthesis of azines

Recently, Dar and et.al reported the grinding-induced approach for the preparation of α aminophosphonates using aluminium pillared interlayered clay under solvent free conditions [17b]. The salient advantages of their research include operational simplicity, greater selectivity, high yields and clean reaction conditions. Therefore, we studied the efficacy of the NH₂-MMT nanocatalyst on the synthesis of azines by grinding technique. To optimize the reaction conditions, the reaction of benzaldehyde (2 mmol) and hydrazine sulfate (1 mmol) was used as a model reaction. First, we investigated the catalytic effect of NH₂-MMT and MMT nanoclay in the synthesis of the azine compounds under grinding method at room temperature and under reflux condition in EtOH as solvent. As Table 1 shows, NH₂-MMT exhibited the highest catalytic activity as compared with MMT in terms of reaction times and product yield. This may be due to the base and acid sites in amine functionalized acidified MMT. Meanwhile, pure MMT acts as a Lewis acid in this process. Another significant observation is that the solvent-free grinding process is more successful considering time and yield than reflux condition in EtOH (Table 1, entry 2 and 3). In order to study the effect of quantity of catalyst on the model reaction,

we carried out the reaction using 0.1, 0.15, 0.20 and 0.25 g of NH₂-MMT nanoclay and found that the optimal NH₂-MMT concentration was 0.20 g in this process (Table 1, entry 5). To demonstrate the efficiency of the chosen nanocatalyst, we carried out a blank reaction (without catalyst) under solvent-free grinding using amine functionalized catalyst (Table 1, entry 1). However, we are getting better results using the heterogeneous catalytic system for a shorter period of time and further increase the yields of products. So we have developed a one-pot procedure using stable and inexpensive nanocatalyst in a extremely simple, facile, and clean solvent-free rapid protocol at room temperature, with excellent yields.

Entry Catalyst (g)		Time (min)	/ Yield ^b (%)	Time (min)/	Time (min)/Yield ^b (%)		
Lintry	Cuturyst (g)	Solvent-free grinding		Reflux co	ondition		
1	-	15	90	25	70		
2	MMT (0.15)	5	90	20	70		
3	NH ₂ -MMT (0.15)	2.5	92	15	85		
4	NH ₂ -MMT (0.10)	3	90	15	80		
5	NH ₂ -MMT (0.20)	2	94	10	90		
6	NH ₂ -MMT (0.25)	2	94	10	90		

Table 1. Optimization of the reaction conditions for the synthesis of azines.^a

^a benzaldehyde (2 mmol), hydrazine sulfate (1 mmol)

^bIsolated yield of the pure compound.

After optimizing the reaction conditions, in order to explore the scope and generality of this method, various aldehydes and ketones were used for the synthesis of azines. The results are shown in Tables 2. These results show that aromatic aldehydes (ketones) with electron-withdrawing group such as 4-Cl afforded the target products in high yields and purity in short time. Aromatic aldehydes with an electron-donating group such as N(Me)₂ reacted sluggishly, which required comparatively longer reaction time with low yield. The activity of aldehydes is higher than ketones, because an aldehyde is less sterically. The position of substituent in the

benzene rings of aldehyde (ketone) influences this reaction. The activity of o-aldehyde is higher than p- and m-benzaldehyde.

.			T• (•)	X [*] 1 lb (a)	(°C)	
Entry	aldehyde/ketone	Product	Time (min)	Y ield ⁶ (%)	m. p (°C)	m.p. (°C) [Rep]
1	benzaldehyde	4a	2	94	93-94	92-93 [30]
2	4-chlorobenzaldehyde	4b	2	96	210-213	213 [31]
3	2-hydroxybenzaldehyde	4c	2	96	213-214	216 [32]
4	4-methylbenzaldehyde	4d	6	9/	159-108	159-161 [32]
5	4-dimethylamino benzaldehyde	4e	8	85	214-215	215 [33]
6	4-methoxybenzaldehyde	4f	8	85	169-170	171 [34]
7	2-fluorobenzaldehyde	4 g	1	98	134-135	132 [35]
8	2,4-dichlorobenzaldehyde	4h	2	95	214-217	213 [35]
9	4-chloroacetophenone	4 i	7	87	214-217	133-134 [36]
10	2-hydroxyacetophenone	4j	5	82	197-199	196-198 [36]
11	4-hydroxyacetophenone	4k	8	80	223-224	223-224 [12]

Table 2. Synthesis of azine derivatives using NH₂-MMT.^a

^a aldehyde (2 mmol), hydrazine sulfate (1 mmol), and NH₂-MMT (0.20 g) under grinding condition at room temperature.

^bIsolated yield of the pure compound.

In scheme 4, a plausible mechanistic pathway is proposed to illustrate the synthesis of azine derivatives catalyzed by NH₂-MMT. As the first step, the NH₂-MMT as base catalyst helps to generate the hydrazine from hydrazonium sulfate. Then, the reaction proceeds *via* the intermediate (**I**), which is formed by the activation of aldehyde carbonyl group by the MMT as acid catalyst, which facilitates the nucleophilic attack of hydrazine to promote the formation of C–N bond to yield intermediate (**II**). The subsequent elimination of water molecule from intermediate (**II**) enhanced by catalyst NH₂-MMT eventually yield compound (**III**) followed by regeneration of the solid acid-base nanocatalyst. The repetition of catalytic loop for compound (**I**) with another aldehyde finally ends up with target azine products.



Scheme 4. Plausible mechanistic pathway for the synthesis of target azine derivatives. This heterogeneous synthetic method is more useful than the protocols published till date, because it has many advantages, such as decreased byproduct formation or without requirement to separate the hydrazone intermediate, reduced pollution, lower cost, and simplicity in processing, which are beneficial to the industry as well as to the environment.

3.3. Catalytic performance of NH₂-MMT in the synthesis of 2-aminothiazoles

The excellent catalytic efficiency of NH₂-MMT in the preparation of azine derivatives motivated us to explore their efficacy for the synthesis of 2-aminothiazole heterocycles. Recently, an efficient method for the synthesis of 2-aminothiazole from thiourea and methylcarbonyls using I₂ in the presence MMT-K10 as a catalyst was developed by our research group.¹⁶ But the usage of I₂ as a iodinating agent, DMSO as solvent and high reaction temperature were still unavoidable in this process. To the best of our knowledge, there is no effective methodology for the synthesis of 2-aminothiazole at room temperature. In this research, we present our studies toward the conversion of iodomethylcarbonyls, which are easily obtained from methylcarbonyls, to the

corresponding 2-aminothiazoles in good to excellent yields using *N*-Iodosuccinimide (NIS) as a halogenating reagent in the presence of NH_2 -MMT as catalyst. We found that NH_2 -MMT provided excellent yields of 2-aminothiazoles by the one-pot of acetophenone, thiourea, and iodine as a model reaction. The results for the optimization of reaction conditions for the synthesis of 2-aminothiazoles are presented in Table 3. The optimized yield was obtained in ethanol medium using 0.1 g NH_2 -MMT (entry 3, Table 3) at room temperature. The reaction without nanocatalyst did not provide satisfactory results under the same conditions (entry 1, Table 3). Althogh, I_2 was an efficient iodination agent for this reaction, but it is a hazardous and toxic reagent and remove it is difficult from the reaction medium.

N-halosuccinimide reagents such as *N*-bromosuccinimide (NBS) and NIS have some specific features that determine their broad application in organic transformations and the halogenation of arenes and heteroarenes under mild conditions. NIS is an iodinating agent that is used for various electrophilic iodinations and as source for iodine in radical reactions. In next experiment, the same reaction was carried out with different iodinating agents in the presence of the same quantity of the NH₂-MMT (entreis 15-23, Table 3). Based on these results, the yield increased with the addition of I₂ and NIS. Therefore, NIS is an efficient and greener iodinating reagent than others (entry 15, Table 3).

 Table 3. Optimization of reaction conditions for the synthesis of 2-aminothiazole using NH2-MMT as a catalyst.^a

Entry	Catalyst (g)	Solvent	Reagent	Yield ^b (%)
1	_	EtOH	I ₂	30
2	0.05	EtOH	I_2	75
3	0.10	EtOH	I_2	97
4	0.15	EtOH	I_2	97

5	0.20	EtOH	I ₂	95
6	0.30	EtOH	I_2	90
7	0.10	H_2O	I_2	65
8	0.10	DMSO	I_2	98
9	0.10	THF	I_2	50
10	0.10	CH ₃ CN	I_2	85
11	0.10	MeOH	I_2	70
12	0.10	EtOAc	I_2	50
13	0.10	CCl_4	I_2	10
14	0.10 (MMT)	EtOH	I_2	50
15	0.10	EtOH	NIS	97
16	0.10	EtOH	HI	75
17	0.10	EtOH	NaI	40
18	0.10	EtOH	KI	40
19	0.10	EtOH	KIO3	50
20	0.10	EtOH	KIO ₄	50
21	0.10	EtOH	NaIO ₄	50
22	0.10	EtOH	HgI ₂	20
23	0.10	EtOH	CH ₃ (CH ₂) ₃ NI	20

^a Reaction conditions: acetophenone (2 mmol), thiourea (3 mmol), and solvent (5 ML) at room temperature for 1h.

^bIsolated yield of the pure compound.

Using optimized one-pot reaction conditions, several 2-aminothiazole derivatives were prepared and the results are given in Table 4. It is clear from results that various methylketones are suitable for this transformation. In the case of aliphatic substrates and aromatic were obtained in good to high yields. The results showed that 2-hydroxy acetophenone has the lowest performance than other methylcarbonyls due to the steric hindrance and the electron donating of hydroxyl group (–OH).

	Ÿ					
Entry	ketone	Product	Time (h)	Yield ^b (%)	m.p (°C)	m.p. (°C) [Rep]
1	Acetaldehyde	3 a	1	90	90-92	89-90 [15a]
2	Acetone		1	90	46-48	45-46 [15a]

Table 4. Synthesis of 2-aminothiazole derivatives in the presence of NH₂-MMT.^a

3	Acetophenone	3b	1	97	151-153	151-153 [15a]	
4	4-Cl-acetophenone	3c	1	98	160-162	161-162 [15a]	
5	4-Br-acetophenone	3d	1	98	180-182	180-183 [15a]	
6	4-OH-acetophenone		1.5	80	197-200	198-200 [15a]	
7	2-OH-acetophenone		2.5	60	138-139	138-139 [15a]	
8	3-Me-acetophenone	3e	1	93	85-88	88-91 [15a]	
9	Ethyl acetoacetate	3g	1.5	95	177-179	177-179 [15a]	
10	Methyl acetoacetate	3h	1.5	92	224-226	225-226 [15a]	
11	Allyl acetoacetate	3i	2	90	148-150	148-149 [15a]	
12	Acetylacetone	3ј	2	92	219-220	219-220 [15a]	
13	Morpholinoacetone		1	98	277-280	272 [34]	

^a Reaction conditions: methylcarbonyl (2 mmol), thiourea (3 mmol), NIS (2 mmol), and NH₂-MMT (0.10 g) in EtOH at room temperature.

^bIsolated yield of the pure compound.

A plausible mechanism for the production of 2-aminothiazoles is presented in scheme 5. In the first step, the acetophenone undergoes the formation of enolate ion under basic conditions using NH₂-MMT as a basic organocatalyst, and enolate converts to α -iodoacetophenone in the presence of NIS. Also, thiourea is converted to enol under basic conditions and react with the iodinated acetophenone for the synthesis of intermediate **I**. Next, the dehydration of **I** followed by the neutralization of H gives the desired [15a].



Scheme 5. Proposed mechanism for the synthesis of 2-aminothiazoles using NH₂-MMT.

Thus, two present methods for C–N bond formation by NH₂-MMT fulfilled the criteria for green synthesis including: (i) this is transition-metal-free C–N bond formation;(ii) it proceeds faster and gives excellent yields at room temperature; (ii) it requires a heterogenization of homogeneous organocatalyst based on MMT clay as a green and eco-friendly nanocatalyst; (iv) it is applicable to a wide range of chemical transformation; (v) the reactions were performed in non-hazardous solvents (EtOH or grinding), non-toxic catalyst and reagent (NIS).

4. Conclusions

In the current study, we have demonstrated a simple, green, and a cost effective one-pot procedure for the synthesis of azines and 2-aminothiazoles in excellent yields at room temperature using an eco-friendly, nontoxic, inexpensive, and chemically highly stable

nanocatalyst. The noteworthy advantages of this method are simplicity of performance, easier work-up procedure, short reaction times and high yields of the products.

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