

Research Article

Copper(II) Anchored on Amine-Functionalized MMT: A Highly Efficient Catalytic System for the One-Pot Synthesis of Bispyrano [2,3-c]pyrazole Derivatives

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In this study, preparation of pyridine-2-carboimine copper complex immobilized on amine-functionalized nanoclay montmorillonite K10 was reported. The products were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and thermogravimetric analysis (TGA). The catalytic activity of this new nanocatalyst, as a natural, renewable, inexpensive, and heterogeneous catalyst, was very effective for the four-component condensation reaction of hydrazine hydrate (or phenyl hydrazine), malononitrile, β -ketoester, and terephthalaldehyde (or isophthalaldehyde) toward the synthesis of multisubstituted bispyrano[2,3-c]pyrazole derivatives. From the viewpoint of green chemistry, the advantages of this approach are accessibility, simplicity, and high yields synthesis. The catalyst was recycled and reused four times without significant loss of activity.

1. Introduction

Today, multicomponent reactions (MCRs) are powerful strategies in organic and medicinal chemistry. Reactions with three or more reactants lead to the products under mild conditions, excellent yield, low costs, high selectivity, and shorter reaction times. Literature shows that there are many reported applications of multicomponent reactions for the synthesis of organic compounds such as Biginelli and Hantzsch reactions [1–7].

During the last decade, pyranopyrazoles played a very important role as precursors of medicine intermediates, fused pyrimidine derivatives, and organic materials. Some of the significant pharmaceutical and medicinal applications are antibacterial [8], antimicrobial [8], anticancer [9], anti-inflammatory [10], and vasodilatory activities [11], herbicidal agents [12], medicinal chemistry [13], pharmaceutical ingredients and biodegradable agrochemicals [14], Chk1 kinase inhibitor, and natural alkaloids.

To the best of our knowledge, limited articles have been reported on the synthesis of bispyrano pyrazole through homogeneous catalysis [15]. There are several disadvantages of homogeneous catalysis including the labor-intensive separation process and recycling. Based on the mentioned issue for homogeneous catalysis, heterogeneous catalysts have become increasingly attractive to scientists. Heterogeneous catalysis has allowed researchers to develop various inorganic-organic functional materials by modifying inorganic hosts with organic molecules. For example, clay minerals constitute a versatile source of inorganic support for the fabrication of advanced inorganic-organic hybrid materials due to their remarkable structural and chemical diversities [16].

Reviewing the existing methods for synthesis of bispyrano[2,3-c]pyrazole derivatives shows that they suffer from prolonged reaction times and the use of nonrecyclable catalysts [17–22]. Considering the disadvantages associated with earlier reported protocols and the increasing

importance of pyranopyrazoles derivatives in pharmaceutical chemistry, there is still a need to develop an efficient, low cost, and ecofriendly protocol for the synthesis of bispyrano[2,3-*c*]pyrazole derivatives under green solid catalytic conditions.

Montmorillonite K10 (MMT K10) has been used due to its potential in absorbing water and other molecules, physicochemical properties, and catalysis activity. MMT K10 as an inorganic solid has been used in organic synthesis as a catalyst and catalysis support. In comparison to the bulk supports, MMT K10 nanoclay offers a large number of potential active sites for the reactants as a result of a large surface-area-to-volume ratio, which eventually results in higher yields [23–31]. Here, we used MMT K10 as a support to provide a new and highly efficient heterogeneous catalytic system consisting of anchored Cu(OAc)₂ by modified imine (MMT-*n*-Pr-NH=Py) as a linker for the synthesis of bispyranopyrazole derivatives (Scheme 1).

2. Experiment

2.1. Chemicals and Apparatus. All chemicals were purchased from 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. FTIR 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° (2θ). The surface morphology of chitosan-based materials was analyzed by field emission scanning electron microscopy (SEM) (EVO LS 10, Zeiss, Carl Zeiss, Germany).

2.2. Catalyst Preparation. According to the previously reported method, the amine-modified montmorillonite (MMT-(CH₂)₃-NH₂) was prepared as follows: 2 g MMT K10 was added to a 15 mL solution of 3-aminopropyltrimethoxysilane (4.8 mmol) in *n*-hexane and the mixture was stirred at room temperature for 3 h. Then, the solvent was removed by filtration, and amine-modified montmorillonite was washed with *n*-hexane, eventually drying under vacuum [32]. Covalent attachment of functional organic groups on the montmorillonite surface has advantages over physisorption and cation exchange. Such compounds would benefit from much higher chemical stability as the guest species would be irreversibly bound to the structure. Grafting is the most viable route for the covalent immobilization of organic functional groups over the surface of montmorillonite [16].

2.3. Synthesis of the Pyridine-2-carboimine Immobilized on Amine-Functionalized MMT K10 (MMT-(CH₂)₃-NH=CHPy). A solution of 2-pyridine carboxaldehyde (2 mmol) in ethanol (5 mL) was added to the MMT-(CH₂)₃-NH₂ (1 g) suspension in ethanol (125 mL) under continuous

stirring at room temperature for 24 h. After filtration, it was washed frequently with ethanol to remove unreacted 2-pyridine carboxaldehyde and dried overnight.

2.4. Synthesis of Copper(II) Anchored on Modified MMT K10 (MMT-[(CH₂)₃-NH=CHPy]-Cu(II)). MMT-(CH₂)₃-NH=CHPy (1 g) was added to the solution containing 1.5 mmol (272 mg) of copper acetate in acetone and stirred at room temperature for 10 h. After being filtered, it was washed thoroughly with acetone and ethanol and dried to yield Cu-anchored by pyridine-2-carboimine immobilized on MMT K10 (Scheme 2).

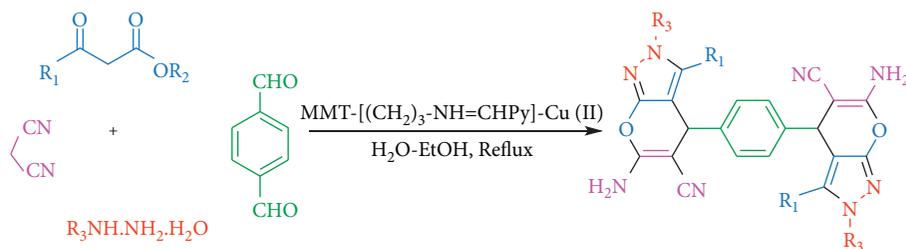
2.5. General Procedure for the Synthesis of Bispyrano[2,3-*c*]pyrazole Derivatives in the Presence of MMT-[(CH₂)₃-NH=CHPy]-Cu(II). A mixture of terephthalaldehyde or isophthalaldehyde (1 mmol), hydrazine hydrate or phenyl hydrazine (2 mmol), β-ketoester (2 mmol), and malononitrile (2 mmol) in the presence of MMT-[(CH₂)₃-NH=CHPy]-Cu(II) (0.01 g) was stirred under reflux conditions for the appropriate time. After completion, as indicated by TLC, the reaction mixture was filtered to separate the catalyst. The filtrate was cooled, and large amounts of a precipitate are formed. The products were purified by recrystallization in hot ethanol. The recovered catalyst was dried and reused for subsequent runs. All the products were characterized by IR, ¹H NMR, and ¹³C NMR and identified by the comparison of the spectral data with those reported in the literature [15].

When a heterogeneous catalyst is used, the recyclability of the catalyst is an important issue. To test this, a series of four consecutive runs of the model reaction with the MMT-[(CH₂)₃-NH=CHPy]-Cu(II) catalyst were carried out. The results are shown in Figure 1.

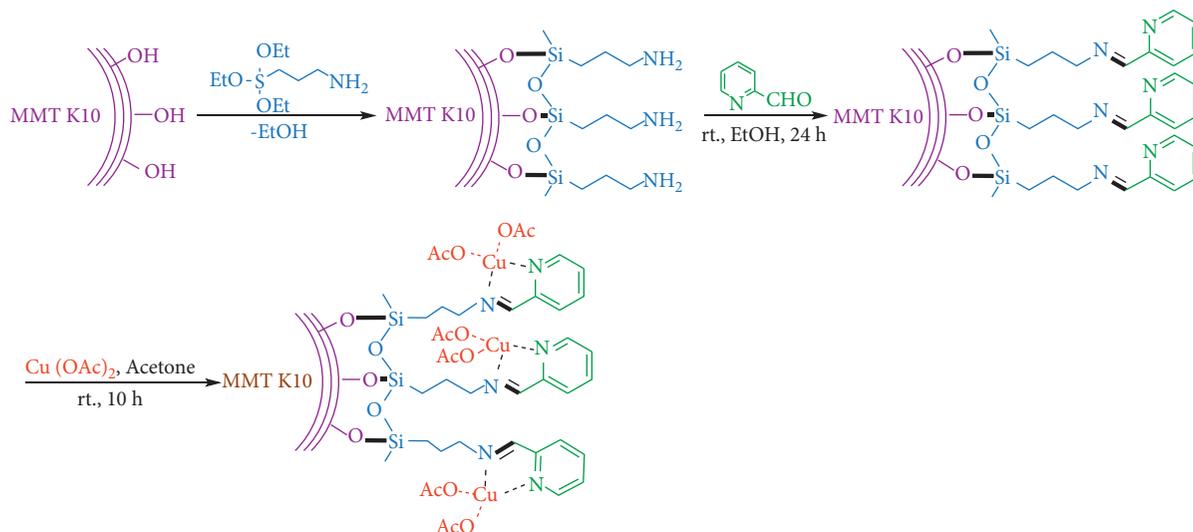
3. Result and Discussion

3.1. Catalyst Characterization

3.1.1. FTIR Spectroscopy. In the first step, the catalyst was analyzed by SEM, XRD, TGA, DTA, EDX patterns, and FTIR. FTIR spectra of the MMT (Figure 2(a)), MMT-NH₂ (Figure 2(b)), MMT-linker (Figure 2(c)), and MMT-[(CH₂)₃-NH=CHPy]-Cu(II) (Figure 2(d)) catalyst are shown in Figure 2. The peaks observed in the area 3432 and 1045 cm⁻¹ refer to Al-OH and Si-O-Si bond stretching vibrations. In the case of intermediate (Figure 2(b)), the peak in 2983 cm⁻¹ (-CH₂- group) confirms that clay is functionalized with (3-aminopropyl)trimethoxysilane (APTMS). The FTIR spectrum of MMT-Cu(II) is shown in Figure 2(c). The peak at 1643 cm⁻¹ which corresponds to the C=N bond represents the propyl group attached to MMT K10. In the case of MMT-[(CH₂)₃-NH=CHPy]-Cu(II) (Figure 2(d)), the C=N stretching frequency is at a lower wavelength of 1624 cm⁻¹ that confirms C=N bond is coordinated to copper through the lone pair of nitrogen in the Schiff base [33].



SCHEME 1: One-pot synthesis of bispyrano[2,3-c]pyrazoles in the presence of copper (II) anchored modified MMT.



SCHEME 2: Preparation of copper(II) anchored on modified MMT K10.

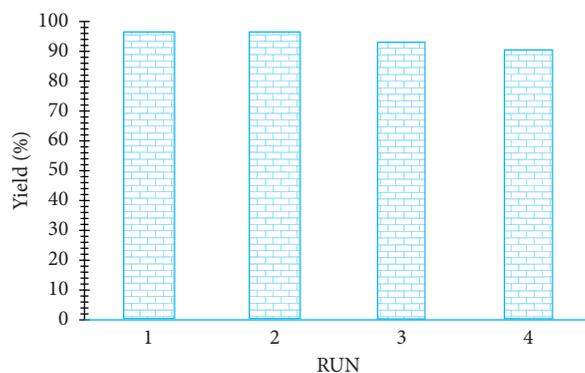


FIGURE 1: Reusability diagram of MMT-[(CH₂)₃-NH=CHPy]-Cu(II) for the model reaction.

3.2. Powder X-Ray Diffraction Analysis. The XRD spectrum of the catalyst is shown in Figure 3. Figure 3(a) shows powder X-ray diffraction (P-XRD) patterns of MMT K10. As can be seen, the positions and relative intensities of all the peaks coincide well with standard XRD patterns that are mainly in the amorphous form. Some peaks which are caused by impurities such as feldspar, cristobalite, and quartz have been detected in all samples of MMT K10. After grafting APTES to the MMT, the distances between the interlayers of MMT-(CH₂)₃-NH₂ were different from MMT K10 (Figure 3(b)). It indicated that the grafting APTES with montmorillonite (MMT-(CH₂)₃-NH₂) increases the

distance between sheets and changes the montmorillonite structures (d-spacing MMT-(CH₂)₃-NH₂ = 11 and d-spacing MMT K10 = 9.64). Following the synthesis of the new catalyst, the characteristic Bragg's peaks were obtained at the same 2θ values which indicate that MMT-(CH₂)₃-NH₂ crystal structure remains stable (Figures 3(c) and 3(d)) [34].

The corresponding EDX analysis confirmed the presence of Cu on the catalyst (8 wt% loadings). During the conversion of MMT-[(CH₂)₃-NH=CHPy] to MMT-[(CH₂)₃-NH=CHPy]-Cu(II), a clear change in sample color was observed (khaki to green), which could be attributed to the presence of copper in the sample (Figure 4).

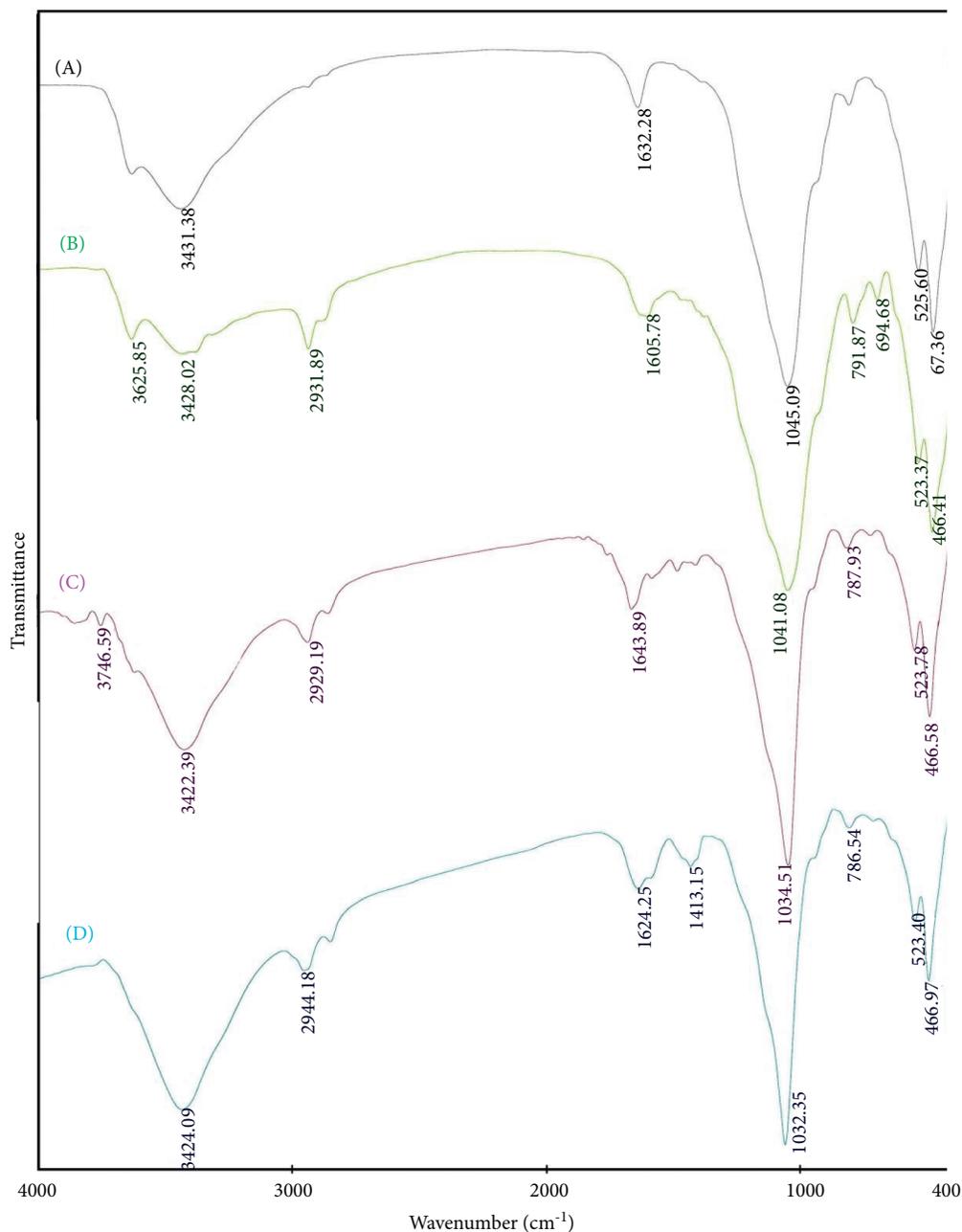


FIGURE 2: FTIR spectra of MMT K10 (a), MMT-[(CH₂)₃-NH₂] (b), MMT-[(CH₂)₃-NH=CHPy] (c), and MMT-[(CH₂)₃-NH=CHPy]-Cu(II) (d).

Figures 5(a)–5(d) show the SEM micrographs of nano-MMT K10, MMT-(CH₂)₃-NH₂, MMT-(CH₂)₃-NH=CHPy, and MMT-[(CH₂)₃-NH=CHPy]-Cu(II). The scanning electron microscopic (SEM) analysis also reveals the sample's surface topography and composition. The morphology of the MMT-(CH₂)₃-NH₂ and MMT-(CH₂)₃-NH=CHPy were almost similar to MMT K10, as can be seen from the inset of Figures 5(b) and 5(c). The micrographs of MMT-(CH₂)₃-NH₂ and MMT-(CH₂)₃-NH=CHPy clearly show highly porous morphology. MMT-[(CH₂)₃-NH=CHPy]-Cu(II) reveals that the particles are agglomerated by Cu loading (Figure 5(d)) when compared to MMT K10 (Figure 5(a)).

Furthermore, the thermal stability of MMT-[(CH₂)₃-NH=CHPy]-Cu(II) was evaluated using thermogravimetric

analysis (TGA) as shown in Figure 6. According to the results of thermogravimetric analysis, weight loss of 20 wt% was recorded for MMT-[(CH₂)₃-NH=CHPy]-Cu(II) between 300°C and 700°C.

After identifying and proving the catalyst structure, further exploration of the catalytic activity of MMT-[(CH₂)₃-NH=CHPy]-Cu(II) for the synthesis of bispyranopyrazoles derivatives was performed (Scheme 1, model reaction).

Initially, we tested the effect of catalyst amounts in H₂O-EtOH solvent, and results are summarized in Table 1. Our results showed that with increasing the catalyst from 0.00 g to 0.02 g, reaction yield improved from 40% to 95% (Table 2, entries 1 and 5). It is also shown that the catalyst concentration plays a major role in this reaction. With increasing

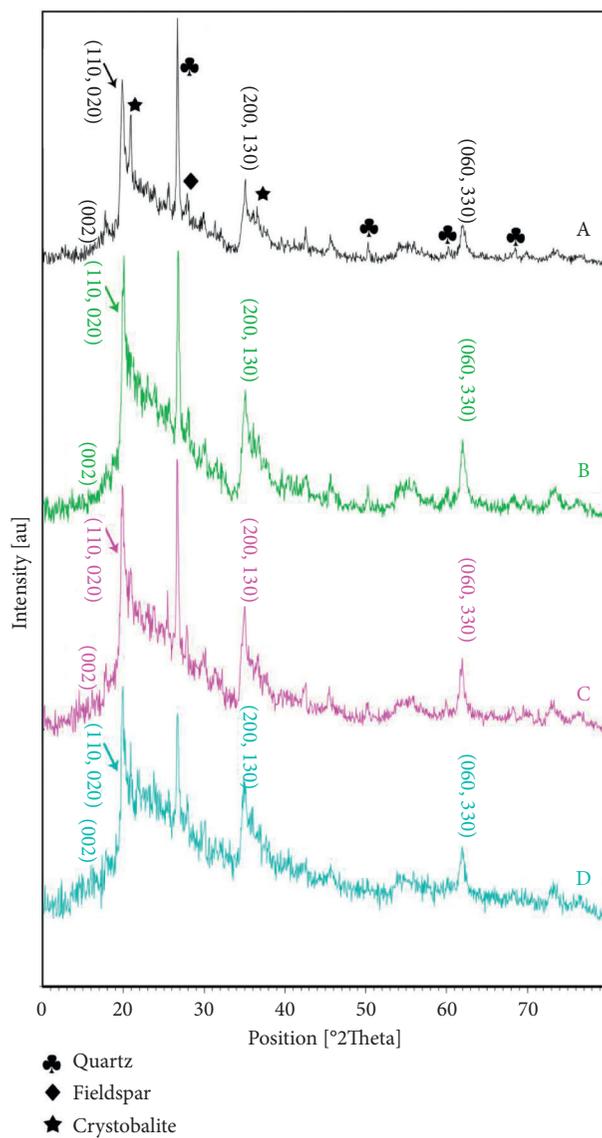


FIGURE 3: X-ray diffraction (XRD) patterns of MMT K10 (a), MMT-[(CH₂)₃-NH₂] (b), MMT-[(CH₂)₃-NH=CHPy] (c), and MMT-[(CH₂)₃-NH=CHPy]-Cu(II) (d).

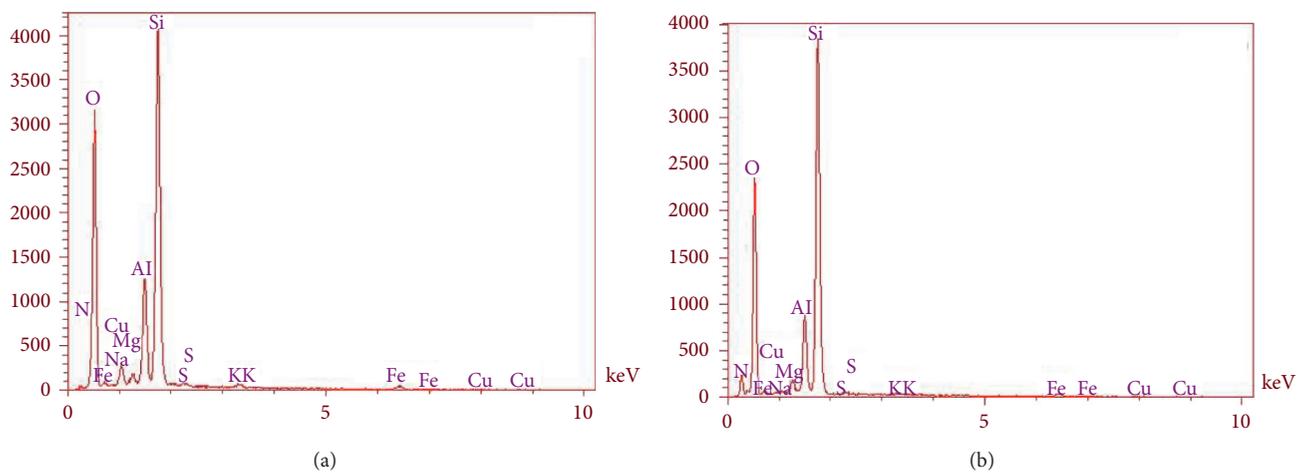


FIGURE 4: Continued.

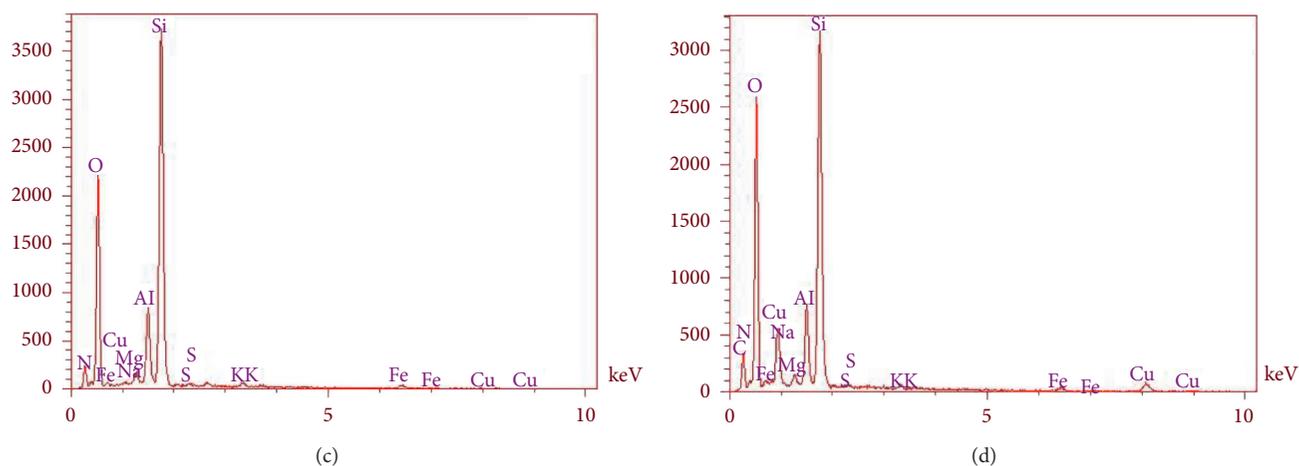


FIGURE 4: EDX spectrum of MMT K10 (a), MMT-[(CH₂)₃-NH₂] (b), MMT-[(CH₂)₃-NH=CHPy] (c), and MMT-[(CH₂)₃-NH=CHPy]-Cu(II) (d).

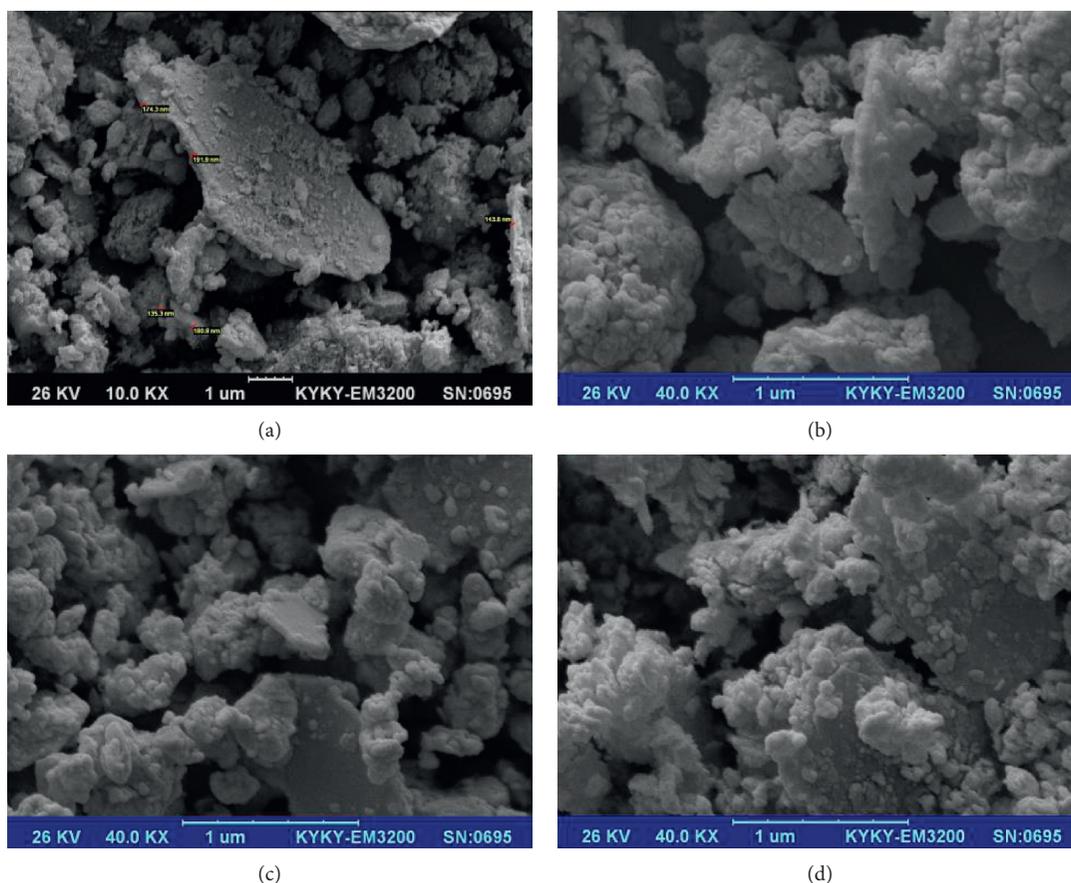


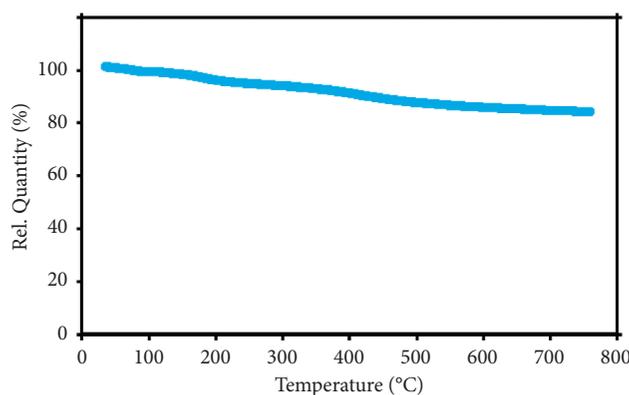
FIGURE 5: SEM images of MMT K10 (a), MMT-[(CH₂)₃-NH₂] (b), MMT-[(CH₂)₃-NH=CHPy] (c), and MMT-[(CH₂)₃-NH=CHPy]-Cu(II) (d).

the amount of catalyst, the reaction yield was unchanged (Table 2, entry 5).

By comparing the condensation of the model reaction in different solvents such as EtOH, MeOH, H₂O-EtOH, and *n*-hexane under reflux condition, the best result was observed in H₂O-EtOH solvent (Table 2, entry 3). Using *n*-hexane as

solvent revealed significantly lower yields, while the other solvents are completely unsuccessful. The results are presented in Table 2.

Eventually, the role of temperature was examined. As indicated in Table 2, increasing the temperature until reflux resulted in a 95% yield (Table 2, entry 4). As

FIGURE 6: TGA thermograms of MMT-[(CH₂)₃-NH=CHPy]-Cu(II).TABLE 1: Comparison of different methods for the synthesis of bispyrano[2,3-*c*]pyrazole using terephthalaldehyde, hydrazine, malononitrile, and ethyl acetoacetate as precursors.

Entry	Catalyst	Temperature (°C)	Solvent	Time (min)	Yield (%)	Reference
1	CeCl ₃	Reflux	EtOH	20	70	[15]
2	Bovine serum albumin	45	H ₂ O-EtOH	60	95	[20]
3	Bael fruit ash	R.T.	H ₂ O	25	90	[21]
4	HMS/Pr-Rh-Zr	80	PEG	15	97	[22]
5	MMT-linker-Cu(II)	Reflux	H ₂ O-EtOH	10	95	Our work

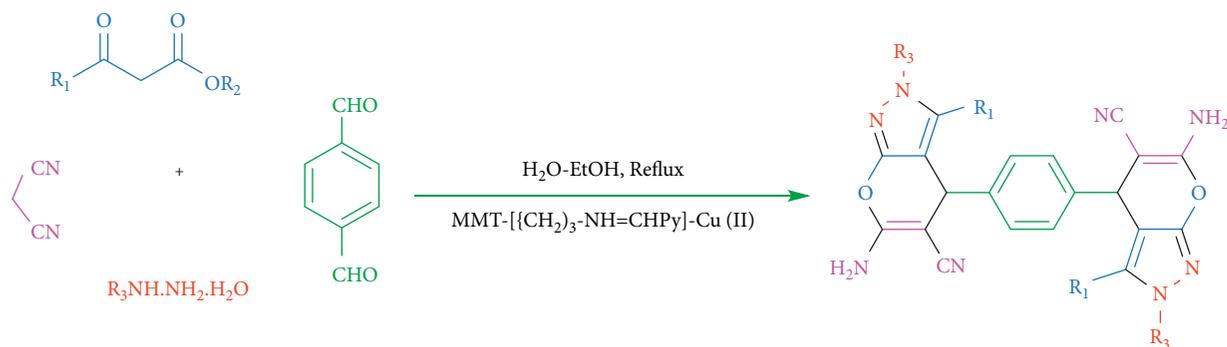
TABLE 2: Results of screening the conditions.

Entry	Amount of catalyst (g)	Temperature (°C)	Solvent	Time (min)	Yield (%)
1	0	Reflux	H ₂ O-EtOH	10	20
2	0.005	Reflux	H ₂ O-EtOH	10	75
3	0.01	Reflux	H ₂ O-EtOH	10	95
4	0.015	Reflux	H ₂ O-EtOH	10	95
5	0.02	Reflux	H ₂ O-EtOH	10	95
6	0.01	Reflux	H ₂ O	10	90
7	0.01	Reflux	EtOH	10	80
8	0.01	Reflux	<i>n</i> -Hexane	10	50
9	0.01	—	—	10	65
10	0.01	100	H ₂ O-EtOH	10	95
11	0.01	50	H ₂ O-EtOH	10	60
12	0.01	25	H ₂ O-EtOH	10	34

temperature increases up to 100°C, the obtained yield was not changed, so the reaction followed at reflux.

In view of these results, we selected the optimized reaction conditions to determine the scope of the model reaction. A wide range of β -ketoesters was subjected to react with terephthalaldehyde (or isophthalaldehyde), hydrazine hydrate (or phenyl hydrazine), and malononitrile in the presence of 0.01 g of the catalyst under reflux condition to generate bispyrano[2,3-*c*]pyrazole derivatives. The results are summarized in Table 3.

Generally, as given in Table 3, terephthalaldehyde gives a better yield rather than isophthalaldehyde. According to the mechanism of the reaction, steric prevention is the reason for this issue (Table 3, entries 5, 6, 9, and 10). Different β -ketoesters were used to prepare bispyrano[2,3-*c*]pyrazole derivatives. When methoxy groups exist instead of ethoxy groups, the reaction is done in a shorter time (Table 3, entries 1, 2, 3, and 4). In addition, it is important to note that when phenyl acetoacetate was used, the yield decreased and the reaction became longer (Table 3, entries 1, 2, 5, and 6). As

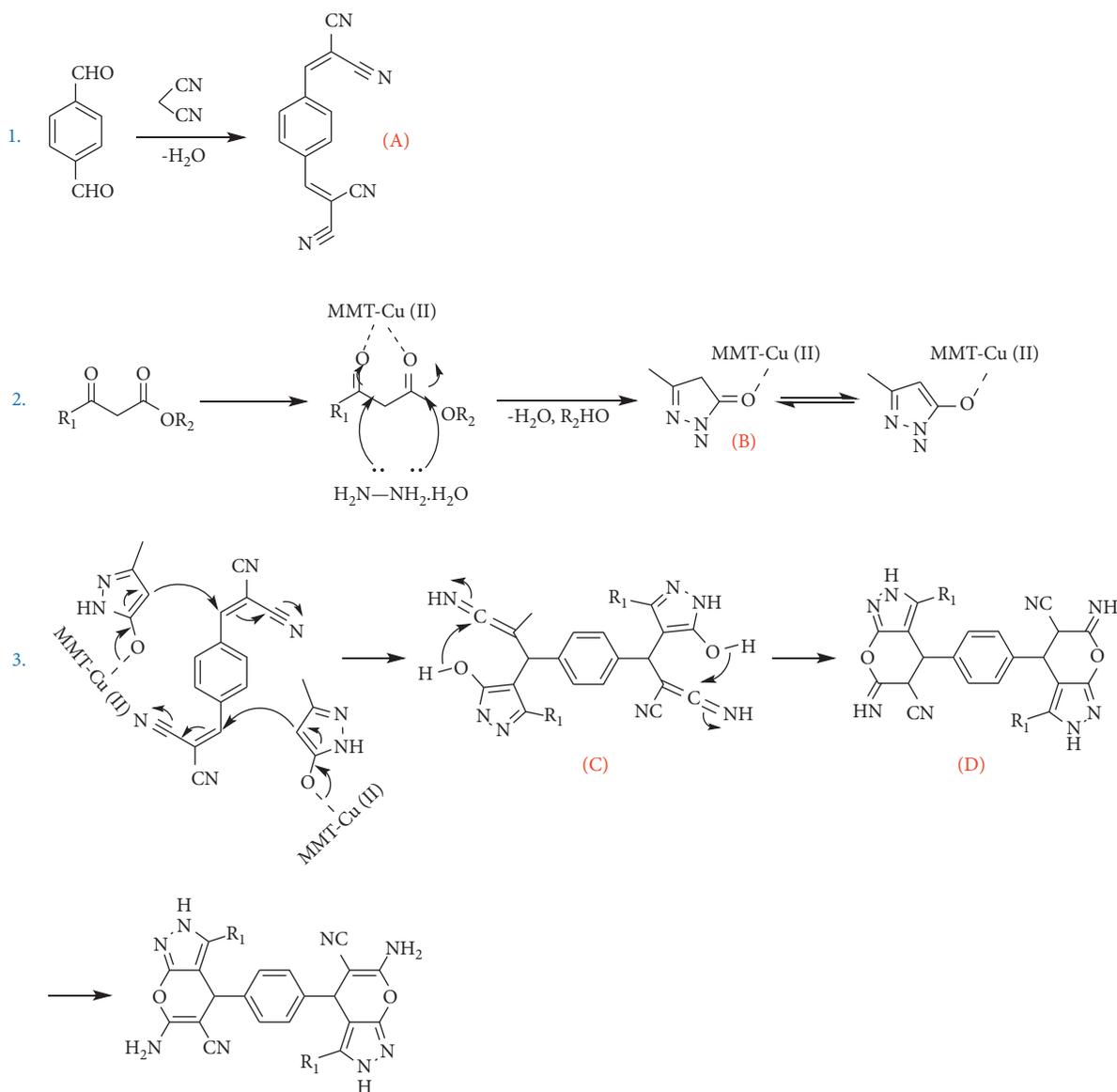
TABLE 3: Using MMT-[(CH₂)₃-NH=CHPy]-Cu(II) in preparation of various of bispyrano[2,3-c]pyrazole derivatives.

Entry	Substrate		Product	Time	Yield (%)
	R ₁ , R ₂	R ₃			
1		NH ₂ NH ₂	5a	10	95
2		NH ₂ NH ₂	5b	5	96
3		PhNHNH ₂	5c	10	92
4		PhNHNH ₂	5d	15	91
5		NH ₂ NH ₂	5e	19	90
6		NH ₂ NH ₂	5f	16	92
7		PhNHNH ₂	5g	30	94
8		PhNHNH ₂	5h	25	90
9		NH ₂ NH ₂	5i	50	85
10		NH ₂ NH ₂	4j	90	45

one additional interesting result, it can be reported that in the case of phenylhydrazine, the reaction is slower than the corresponding hydrazine hydrate (Table 3, entries 1, 2, 3, and 4).

A proposed mechanism for this reaction is illustrated in Scheme 3. At first, the Knoevenagel condensation between

terephthalaldehyde and malononitrile affords intermediate A. On the other hand, condensation of β -ketoester with hydrazine hydrate forms intermediate B. Then, the Michael reaction between intermediates A and B yields C. Finally, in the nucleophile addition of the -OH group on the C=N, the product forms via tautomerization of D.



SCHEME 3: Proposed mechanism for one-pot synthesis of bispyrano[2,3-c]pyrazoles by MMT-[(CH₂)₃-NH=CHPy]-Cu(II).

4. Conclusions

We have developed a new and efficient catalyst for the synthesis of bispyrano[2,3-c]pyrazole derivatives. The catalyst has been recycled and reused five times for the reaction without losing its activity. This catalyst is environmentally friendly, has a simple synthesis and workup procedure and high synthesis yield, and has a short reaction time.

Data Availability

The products that are used to provide the data supporting the findings of this study were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and thermogravimetric analysis (TGA).

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Acknowledgments

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