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Cu(II) immobilized on poly(guanidine-sulfonamide)-functionalized Bentonite@MgFe₂O₄: a novel magnetic nanocatalyst for the synthesis of 1,4-dihydropyrano[2,3-*c*]pyrazole†

 Sedigheh Alavinia, Ramin Ghorbani-Vaghei, * Ramin Ghai and Alireza Gharekhani

In this paper, we aim at synthesizing a new nanocomposite material in which bentonite acts as a nucleation site for MgFe₂O₄ nanoparticles precipitation in the attendance of an external magnetic field (MgFe₂O₄@Bentonite). Moreover, poly(guanidine-sulfonamide), as a novel kind of polysulfonamide, was immobilized on the surface of the prepared support (MgFe₂O₄@Bentonite@PGSA). Finally, an efficient and environment-friendly catalyst (containing nontoxic polysulfonamide, copper, and MgFe₂O₄@Bentonite) was prepared by anchoring a copper ion on the surface of MgFe₂O₄@Bentonite@PGSAMNPs. The synergic effect of MgFe₂O₄ magnetic nanoparticles (MNPs), bentonite, PGSA, and copper species was observed while conducting the control reactions. The synthesized Bentonite@MgFe₂O₄@PGSA/Cu, which was characterized using energy-dispersive X-ray spectroscopy (EDAX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and Fourier-transform infrared (FT-IR) spectroscopy, was applied as a highly efficient heterogeneous catalyst to synthesize 1,4-dihydropyrano[2,3-*c*] pyrazole yielding up to 98% at 10 minutes. Excessive yield, quick reaction time, using water solvent, turning waste to wealth, and recyclability are the important advantages of the present work.

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1 Introduction

Multicomponent reactions (MCRs), in which three or more compounds are combined together to prepare a product, are a straightforward and atom-economic synthetic approach that suggests notable advantages over conventional multistep reaction sequences.^{1–3} In these protocols, the whole range of compounds could be synthesized by minimizing waste, time, and cost without intermediate isolation.^{4–6} Mostly, MCRs exhibit several advantages such as speed, simple workup, environment friendliness, short reaction times, higher yields, use of non-toxic solvents, and no use of column chromatography for purification.^{7–10} In recent years, many publications based on MCRs have been reported, which emphasizes their highlighted applications in organic and medicinal chemistry.^{11–14}

1,4-Dihydropyrano[2,3-*c*]pyrazole is a specific heterocyclic pharmacophore with diverse medicinal chemistry and several interesting pharmacological and therapeutic characteristics.^{15–18} Moreover, it is used as the core moiety to prepare many well-known drugs having antifungal, anti-

inflammatory, antitumor, and several other pharmaceutical and bioorganic features (Fig. 1).

Recently, several catalytic systems have been developed to enhance the reaction conditions. Notably, each technique involves specific advantages and opens a new horizon in synthesizing 1,4-dihydropyrano[2,3-*c*] pyrazole^{18–25} (Scheme 1). Nevertheless, such catalytic systems have shortcomings such as long reaction time, tedious workup, difficult reusability and recovery of precious metal catalysts, and environmental hazards.

Regarding the growing interest of organic chemists in nanocomposites, several studies have been conducted on these materials due to the unique surface and physical properties of these heterogeneous catalysts in different organic reactions.^{26–31} Nowadays, magnetic nanoparticles, which are one of the most influential factors in the nanomaterial family, have been extensively employed in different sciences, consisting of drug shipping, sickness recognition, water desalination, and chemical catalysis.^{3,31} Among magnetic nanoparticles, nanophase spinel ferrites with superparamagnetic behavior are presently utilized in drug transport, microwave devices, catalytic activity, and magnetic imaging.^{4,32–35} As valuable materials, ferrites are compounds with different and useful physical properties along with high chemical stability and low production cost.³⁶ Among diverse structures, spinel ferrites are the most important class

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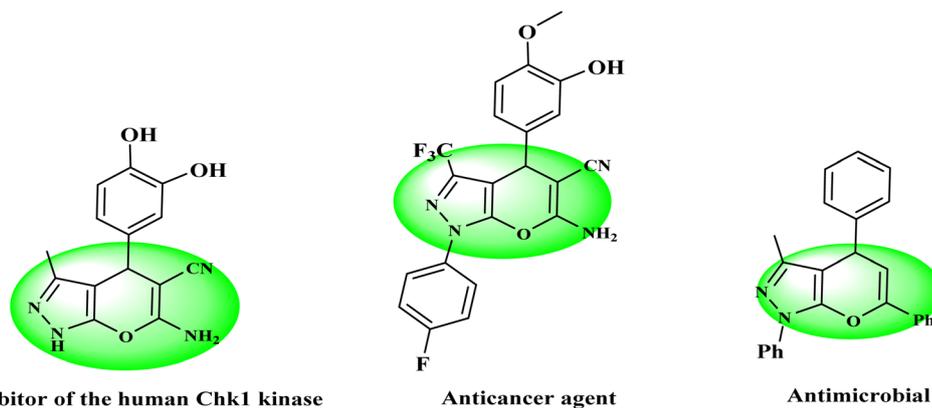
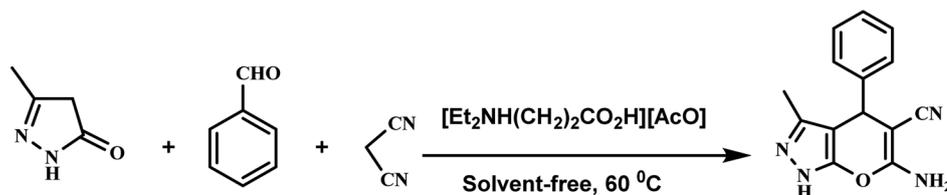
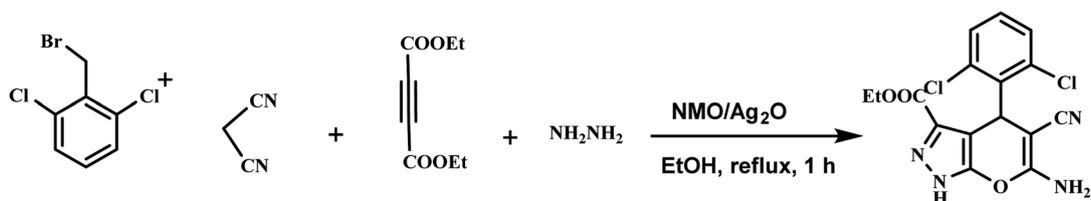


Fig. 1 Selective examples of pharmaceutically important 1,4-dihydropyranopyrazole.

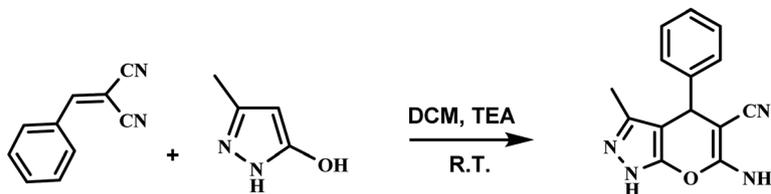
M.A. Shaikh²¹ (2018)



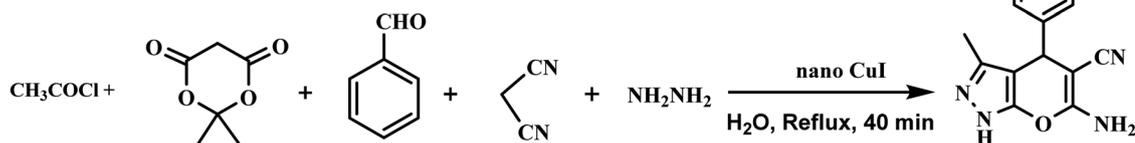
M. Beerappa²² (2017)



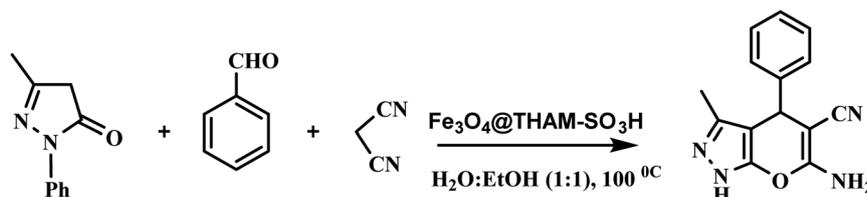
H. Kashtoh²³ (2016)



J. Safaei-Ghomi²⁴ (2013)



H.F. Niya²⁵ (2020)



Scheme 1 Recent methods for the synthesis of 1,4-dihydropyranopyrazole.



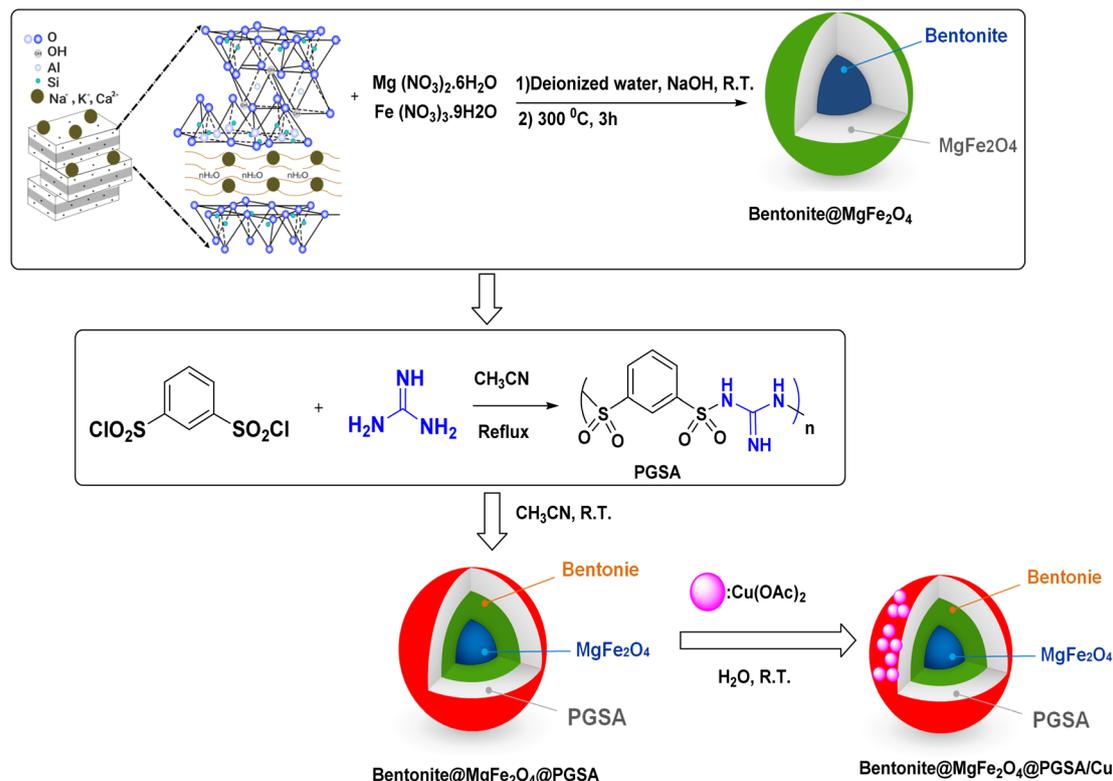


Fig. 2 Schematic representation of the synthesized Bentonite@MgFe₂O₄@PGSA/Cu nanocomposite.

and are divided into normal and inverse forms, in which Mg/Fe₂O₄ has great applicability owing to its potential for use in different fields.^{37,38} In this regard, the functionalization of ferrite-based nanocomposites is a useful method to improve the physicochemical features and compatibility. Ferrite magnetic nanoparticles can be functionalized with organic and inorganic compounds such as rice husk, ash, chitosan, activated carbon, and clay materials to synthesize nanocomposites based on ferrites.^{29,39–41}

Clay materials, such as quartz, talc, calcite, and dolomite, have three-dimensional porous frameworks, tunable surface functionalities, large surface area, and pore channels with regular geometry.^{40–42} Because of their inherent advantages, clays have been widely used in constructing biomedicine, chemical sensing, heterogeneous catalysts, and dye adsorption.⁴³ Therefore, synthesizing magnetic clay to develop atom-economic reactions and reduce negative environmental impact can be a useful process.

In this regard, magnetic clay is a promising inorganic compound incorporated in a polymer matrix to synthesize a polymer/clay nanocomposite.^{28,44} However, this system offers low compatibility between the polymer and clay, leading to a defective structure and irregular morphology. In this respect, the choice of the polymer and clay matrix pair is very important in polymer/clay construction regarding its role in their performance and morphology.

Polysulfonamides are among the other highly-interesting compounds used in medicinal chemistry and to prepare

heterogeneous catalysis.⁴⁵ Polysulfonamides have good chemical stability, great surface area, and low skeleton density.^{45–47} The final structure of the polysulfonamides was controlled by the appropriate selection of the monomers. In this sense, guanidine has been used to prepare a novel organic polymer support (PGSA) (Fig. 2).

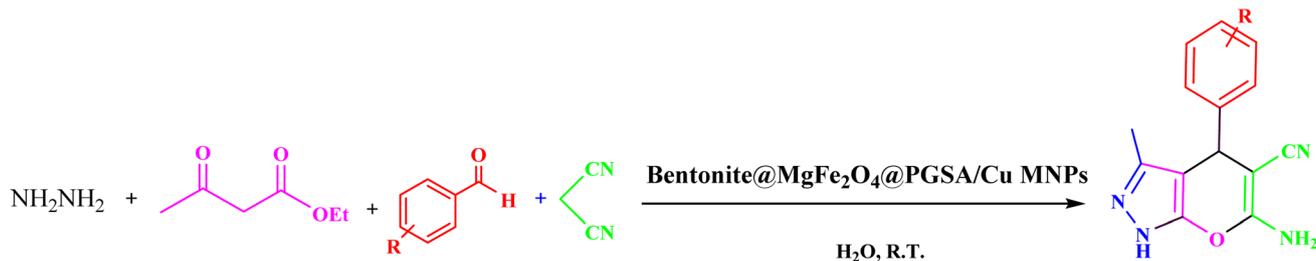
Herein, regarding the abovementioned points and following our current efforts in exploring green catalytic protocols toward chemical synthesis, a new organometallic nanocatalyst is synthesized, which consists of magnetic bentonite and PGSA and offers the advantages of both materials. Furthermore, the problem of separation was directly solved in a sense that the number of active sites having nanomagnetic features increased. Copper ions were then successfully decorated on the prepared support (Bentonite@MgFe₂O₄@PGSA/Cu) (Fig. 2). Eventually, the nanocatalyst was successfully incorporated in a three-component reaction to prepare the new pyrano[2,3-*c*]pyrazoles. This pharmaceutically valuable nanocatalyst was fabricated through mild reaction conditions using H₂O with short reaction times (Scheme 2). Notably, this study is the first report on the catalytic application of Bentonite@MgFe₂O₄@PGSA/Cu MNPs.

2 Experimental

2.1. Chemicals and instruments

All the chemicals, reagents, and equipment used in this study are listed in Table 1.





Scheme 2 Synthesis of 1,4-dihydropyrano[2,3-c]pyrazole derivatives using Bentonite@MgFe₂O₄@PGSA/Cu nanocomposite.

Table 1 Chemicals and equipment used in this study

Materials and equipment	Purity and brand
Bentonite stone	Sigma Aldrich (≥99.995%)
Guanidine	Sigma Aldrich (99.9%)
FeCl ₂ ·4H ₂ O	Sigma Aldrich (98%)
FeCl ₃ ·6H ₂ O	Sigma Aldrich (≥98%)
K ₂ CO ₃	Merck (98%)
Sodium hydroxide	Merck (97%)
Ethanol	Sigma Aldrich (97%)
Acetonitrile	Merck (98%)
Sodium borohydride	Sigma Aldrich (≥96%)
FT-IR analysis	Shimadzu IR-470 spectrometer
EDX analysis	Numerix DXP-X10P
SEM analysis	Sigma-Zeiss microscope
TEM analysis	Phillips Cm 12 instrument
XRD analysis	JEOL JDX-8030 (30 kV, 20 mA)
NMR analysis	Varian Unity Inova 500 MHz
Ultrasound cleaning bath	KQ-250 DE (40 kHz, 250 W)
Melting point measurement	Electrothermal 9100, made in UK

2.2. Preparation of Bentonite@MgFe₂O₄ NCs

MgFe₂O₄-bentonite nanoparticles were prepared through a hydrothermal method using 8.7 mmol ferric nitrate, 8.7 mmol magnesium nitrate, and bentonite (1 g) in an aqueous solution pH 12 (adding sodium hydroxide (1 M)), which was then stirred for 1 h. Afterward, black nanoparticles were separated using an external magnet, washed with distilled water and dried at 80 °C overnight. The prepared catalyst was calcined in a muffle furnace at 300 °C for 3 h (Fig. 2).

2.3. General procedure for the synthesis of poly(guanidine-sulfonamide) (PGSA)

Benzene-1,3-disulfonyl chloride (10 mmol) was added to 5 mL acetonitrile, and then, guanidine (20 mmol in 5 mL CH₃CN) was added dropwise to the initial mixture and stirred under reflux condition for about 6 h (Fig. 2).

2.4. Bentonite@MgFe₂O₄@PGSA/Cu synthesis

The functionalization of Bentonite@MgFe₂O₄ was done *via* PGSA coating on the surface of Bentonite@MgFe₂O₄. In this regard, 1.0 g PGSA was dispersed in 100 mL acetonitrile, which was followed by the addition of Bentonite@MgFe₂O₄ (1.0 g). Besides, it was at room temperature that the reaction mixture was stirred for 4 h. Afterward, the resulting mixture was filtered out and washed with acetonitrile (10 mL). Subsequently, the

synthesized support (1.0 g) was dispersed in 50 mL H₂O using an ultrasonic bath (15 min). Thereupon, 0.5 g Cu(OAc)₂ was dissolved in 5 mL H₂O and then it was added to the previous mixture. After stirring the mixture for 5 h, the resulting precipitate was separated and washed with 50 mL H₂O and, finally, it was dried in an oven (Fig. 2).

2.5. General procedure for the synthesis of substituted 1,4-dihydropyrano[2,3-c]pyrazole derivatives

Benzaldehyde (1 mmol), malononitrile (1 mmol), ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), and Bentonite@MgFe₂O₄@PGSA/Cu (10 mg, 0.2 mol%) were stirred in water solvent at room temperature. After the completion of the reaction (monitored by TLC), Bentonite@MgFe₂O₄@PGSA/Cu catalyst was isolated by an external magnet, washed with EtOH and EtOAc (2 × 5 mL), and dried under vacuum. The title compounds were obtained in their crystalline forms by the recrystallization of ethanol solution (Scheme 1).

3 Results and discussion

3.1. Characterization of Bentonite@MgFe₂O₄@PGSA/Cu nanocomposite

Fig. 3 illustrates the Fourier transform infrared (FT-IR) spectra of PGSA, Bentonite@MgFe₂O₄, Bentonite@MgFe₂O₄@PGSA,

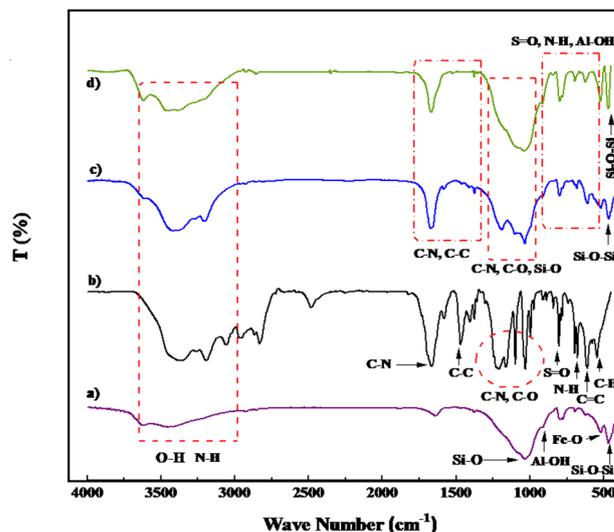


Fig. 3 FT-IR spectra of (a) Bentonite@MgFe₂O₄, (b) PGSA, (c) MgFe₂O₄@Bentonite@PGSA, (d) MgFe₂O₄@Bentonite@PGSA/Cu.



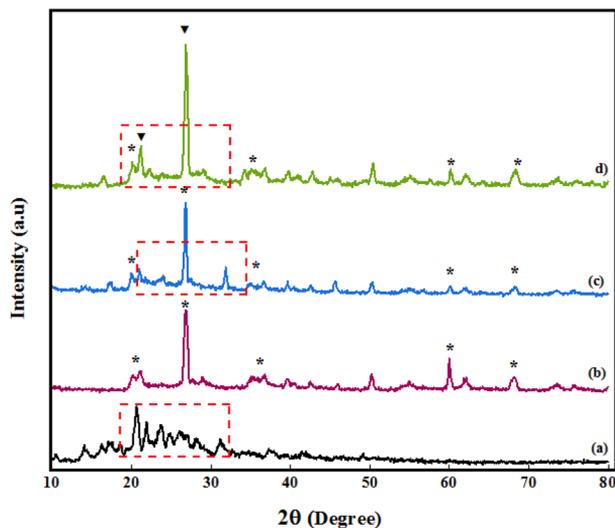


Fig. 4 XRD spectrum of (a) PGSA, (b) Bentonite@MgFe₂O₄, (c) Bentonite@MgFe₂O₄@PGSA, (d) Bentonite@MgFe₂O₄@PGSA/Cu.

and Bentonite@MgFe₂O₄@PGSA/Cu nanocomposite. Regarding the Bentonite@MgFe₂O₄ spectrum, the absorption bands at 471, 520, 780, 926, and 1055 cm⁻¹ belong to the tensile vibrations of the Si–O–Si, Fe–O, Mg–O, Al–OH, and Si–O bonds, respectively (Fig. 3a). Considering the FT-IR spectrum of PGSA, the broad band at 3200–3700 cm⁻¹ indicates the presence of NH and NH₂. The vibration bands at 1338 and 1160 cm⁻¹ (because of the O=S=O stretching) demonstrate the presence of sulfone bridges in the PGSA. Furthermore, the absorption bands at 1664 and 1682 cm⁻¹ indicate the presence of guanidine (Fig. 3b). According to the spectral information of Bentonite@MgFe₂O₄ and PGSA, it was observed that in the Bentonite@MgFe₂O₄@PGSA spectrum (Fig. 3c), all tensile vibrations of PGSA and Bentonite@MgFe₂O₄ have appeared. Finally, regarding the Bentonite@MgFe₂O₄@PGSA/Cu nanocomposite spectrum (Fig. 3d), the interaction between the support and Cu shifted the C–N vibration to about 1675 cm⁻¹ (1685–1675 cm⁻¹). The results from the comparison of the FT-IR spectra propose that

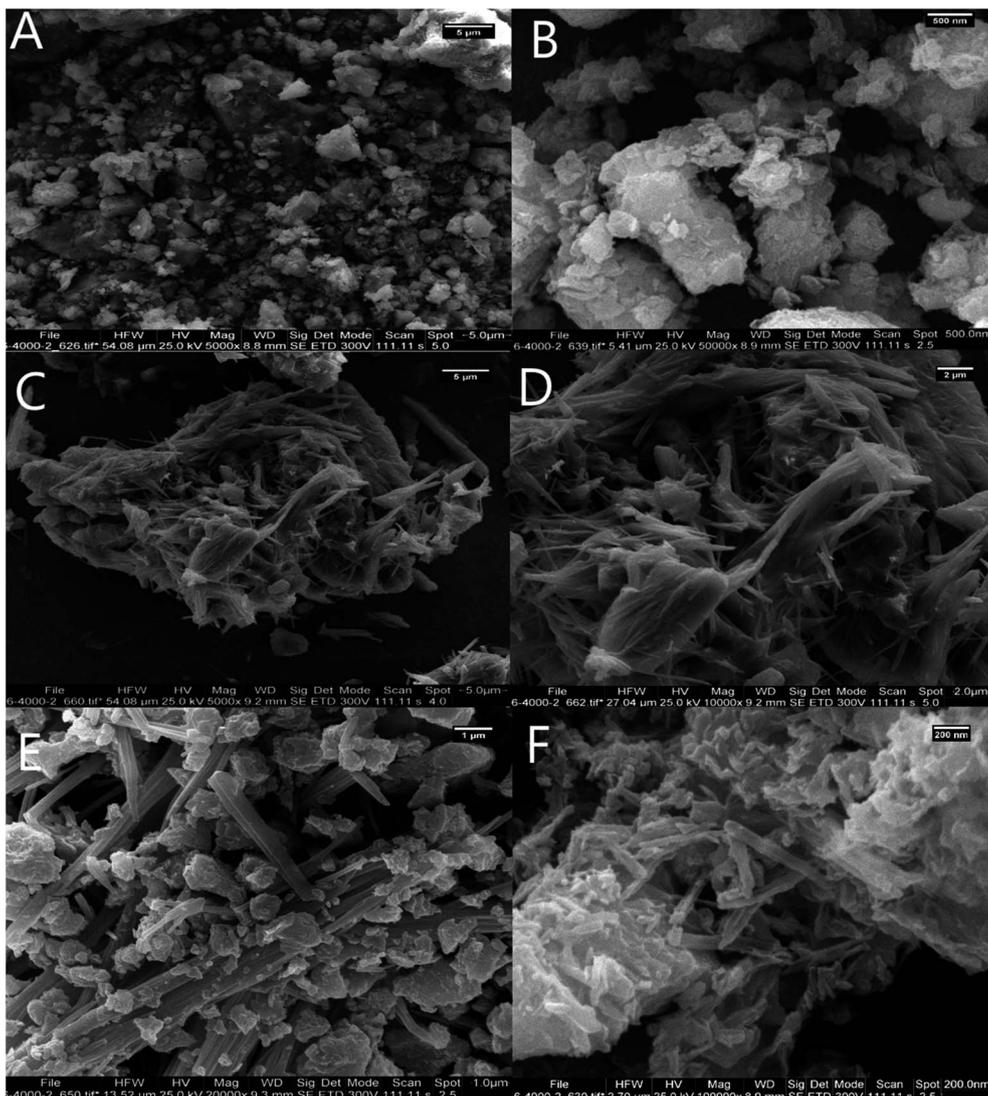


Fig. 5 FESEM image of (A and B) Bentonite, (C and D) PGSA, (E) Bentonite@MgFe₂O₄@PGSA, (F) Bentonite@MgFe₂O₄@PGSA/Cu.



PGSA and copper have been successfully loaded on the surface of Bentonite@MgFe₂O₄.

Structural identification of PGSA, Bentonite@MgFe₂O₄, Bentonite@MgFe₂O₄@PGSA, and Bentonite@MgFe₂O₄@PGSA/Cu nanocomposite systems was also carried out using XRD analysis (Fig. 4). Considering the XRD pattern of PGSA, the diffraction peaks at $2\theta = 27.8^\circ$, 29.72° , and 30.67° are related to the triazine, guanidine, and sulfonamide groups, respectively, and have good crystalline properties (Fig. 4a). Regarding the XRD pattern of Bentonite@MgFe₂O₄, the diffraction peaks at $2\theta = 23^\circ$ and 28° can be attributed to bentonite, and the peaks at 61° and 69° belong to MgFe₂O₄. Moreover, Fig. 4c shows the XRD pattern of Bentonite@MgFe₂O₄@PGSA. The observed peaks indicate PGSA layers around Bentonite@MgFe₂O₄, confirming the formation of the Bentonite@MgFe₂O₄@PGSA core-shell (Fig. 4c). Regarding the Bentonite@MgFe₂O₄@PGSA/Cu nanocomposite, the immobilization of copper ion on Bentonite@MgFe₂O₄@PGSA does not affect the crystal structure of Bentonite@MgFe₂O₄. In this figure, distinct peaks in $2\theta = 21.4$ and 28.3° regions are indexed to copper metal that overlaps with peaks related to PGSA (Fig. 4d).

The FESEM images of Bentonite@MgFe₂O₄ (Fig. 5A and B) revealed the existence of spherical MgFe₂O₄ NPs over the bentonite matrix. Notably, the average grain size was 20–35 nm. The FE-SEM image indicates the layered structure of PGSA (Fig. 5C and D). The FE-SEM image of

Bentonite@MgFe₂O₄@PGSA shows the layered structure of PGSA, as formed on the surface of MgFe₂O₄@Bentonite nanocomposite. The presence of PGSA is an essential factor to prevent agglomeration. The figure shows the coexistence of Bentonite@MgFe₂O₄ and PGSA on the surface of the prepared catalyst (Fig. 5E). The surface morphology of Bentonite@MgFe₂O₄@PGSA/Cu is shown in Fig. 5F. This figure shows the coexistence of Bentonite@MgFe₂O₄ and PGSA on the surface of the prepared catalyst. Significantly, the distribution of copper ions on the surface of Bentonite@MgFe₂O₄@PGSA did not change the support morphology.

The size distribution of Bentonite@MgFe₂O₄@PGSA/Cu MNPs was investigated using transmission electron microscopy (TEM) (Fig. 6A–D). The TEM images of Bentonite@MgFe₂O₄@PGSA/Cu MNPs show some specific aggregation (Fig. 6A and B), probably due to the magnetic nature of MgFe₂O₄, which indicates that the coatings were not much effective in stopping the aggregation. Overall, these observations confirm the successful coating of PGSA (the bright area) on Bentonite@MgFe₂O₄ (*i.e.*, the dark area). Besides, a sharp gap between the support and shell proves the support's spherical solid morphology. Furthermore, a stacking texture with slight aggregation is developed regarding the interparticle magnetic attractions. At the same time, copper loading did not change the support morphology, and the prepared catalyst showed some features of the crystalline structure.

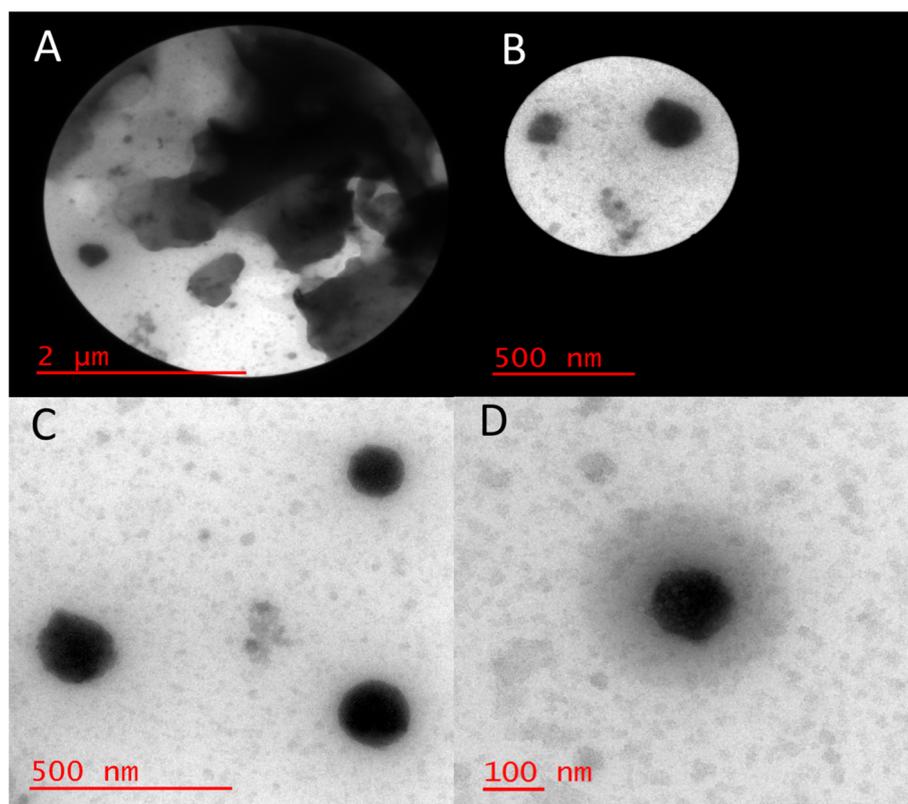


Fig. 6 HRTEM image of Bentonite@MgFe₂O₄@PGSA/Cu MNPs at different scale 2 μ m (A), 500 nm (B and C), 100 nm (D).



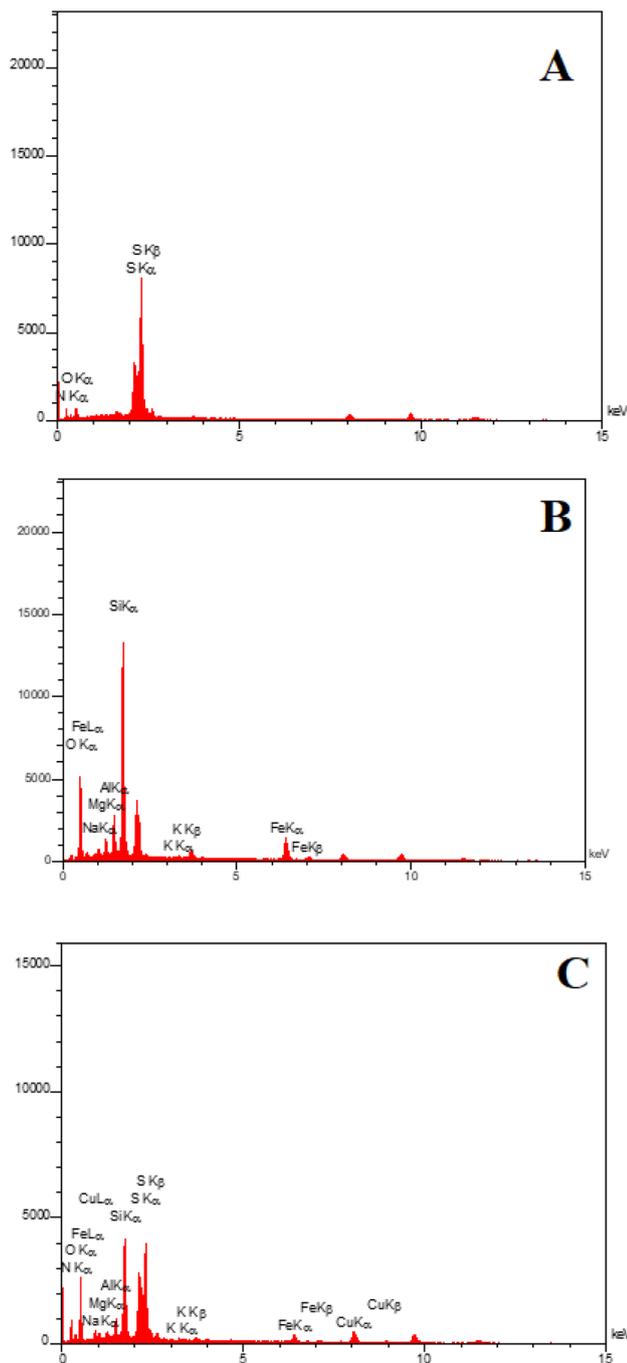


Fig. 7 EDX spectrum of (A) PGSA, (B) Bentonite@MgFe₂O₄, (C) Bentonite@MgFe₂O₄@PGSA/Cu nanocomposite.

EDAX analysis confirmed the presence of C, N, O, and S elements for PGSA (Fig. 7A) and Fe, O, Mg, and Al for Bentonite@MgFe₂O₄ (Fig. 7B). The EDX analysis of Bentonite@MgFe₂O₄@PGSA/Cu nanocomposite confirms the presence of all studied elements (Fig. 7C). The elemental mapping study of Bentonite@MgFe₂O₄@PGSA/Cu MNPs indicates the uniform distribution of elemental components in the prepared structure (Fig. 8).

Fig. 9 illustrates the ¹H NMR spectra of PGSA. The peaks corresponding to the aromatic groups appear in the range of 7.06–7.62 ppm, while the amine peaks appear in the range of 7.96–8.26 ppm.

3.2. Application of Bentonite@MgFe₂O₄@PGSA/Cu

As shown in Table 2, *p*-chlorobenzaldehyde, malononitrile, ethyl acetoacetate, and hydrazine hydrate were used as substrates for the optimization study. Initially, based on our observations, in the absence of the catalyst, the reaction could not proceed even after a long reaction time (entry 1). Then, the effect of several solvents, *i.e.*, DMF, toluene, ethanol, and the solvent-free ones, has been also screened. The reaction proceeded in toluene with a good yield of the product (68%). Water, the best choice for this reaction, yielded the product at up to 98%. Using DMF and EtOH as the solvent decreased the yield (entries 2–6). This superior catalytic performance of Bentonite@MgFe₂O₄@PGSA/Cu in water can be attributed to the amphiphilic behavior of the surface multifunctionalization of Bentonite@MgFe₂O₄ using polyguanidinesulfonamide units. The examination of various catalyst loadings (entries 7–8) revealed that 0.1 mol% (entry 5) was optimal for the best catalytic results. Finally, Bentonite@MgFe₂O₄@PGSA, Bentonite@MgFe₂O₄, and PGSA were investigated to compare their catalytic performance. However, moderate yields are related to the effect of functionalization (entries 9–12).

The generality and scope of the reaction were explored on numerous aldehydes under the optimum conditions, the results of which are given in Table 3. In this sense, the electron-withdrawing groups on aromatic aldehydes yielded the desired alcohols in high yields and high reaction rates (entries 1–5). Although the electron-donating groups also led to high yielded additions, the rates of conversion were higher (entries 6–8). Moreover, this methodology was successfully used for hetero-aromatic benzaldehydes such as thiophene-2-carbaldehyde, furfural, and isonicotinaldehyde (entries 9–11), producing the corresponding product in excellent yield without forming any byproduct. Furthermore, reactions with 2-naphthaldehyde and [1,1'-biphenyl]-4-carbaldehyde afforded the corresponding products in high yields (entries 12–13).

3.3. Investigation of the mechanism of the reaction

The Knoevenagel reaction has been successfully employed as a starting point for many multicomponent reactions. At the beginning of the reaction, Bentonite@MgFe₂O₄@PGSA/Cu activates the carbonyl groups in the 1,3-dicarbonyl compound and then hydrazine hydrate attacks the activated carbonyl groups to generate pyrazolone (I), which was further rearranged into tautomer (II) *via* keto–enol tautomerization. Afterward, the Bentonite@MgFe₂O₄@PGSA/Cu Lewis acid catalyzed the Knoevenagel condensation of aryl aldehydes with active methylene compound (malononitrile), followed by the elimination of a water molecule to produce an α,β -unsaturated intermediate (III). Subsequently, Michael 1,4-addition (or conjugate addition) reaction between tautomer (II) and the activated intermediate (III) is facilitated to form intermediate



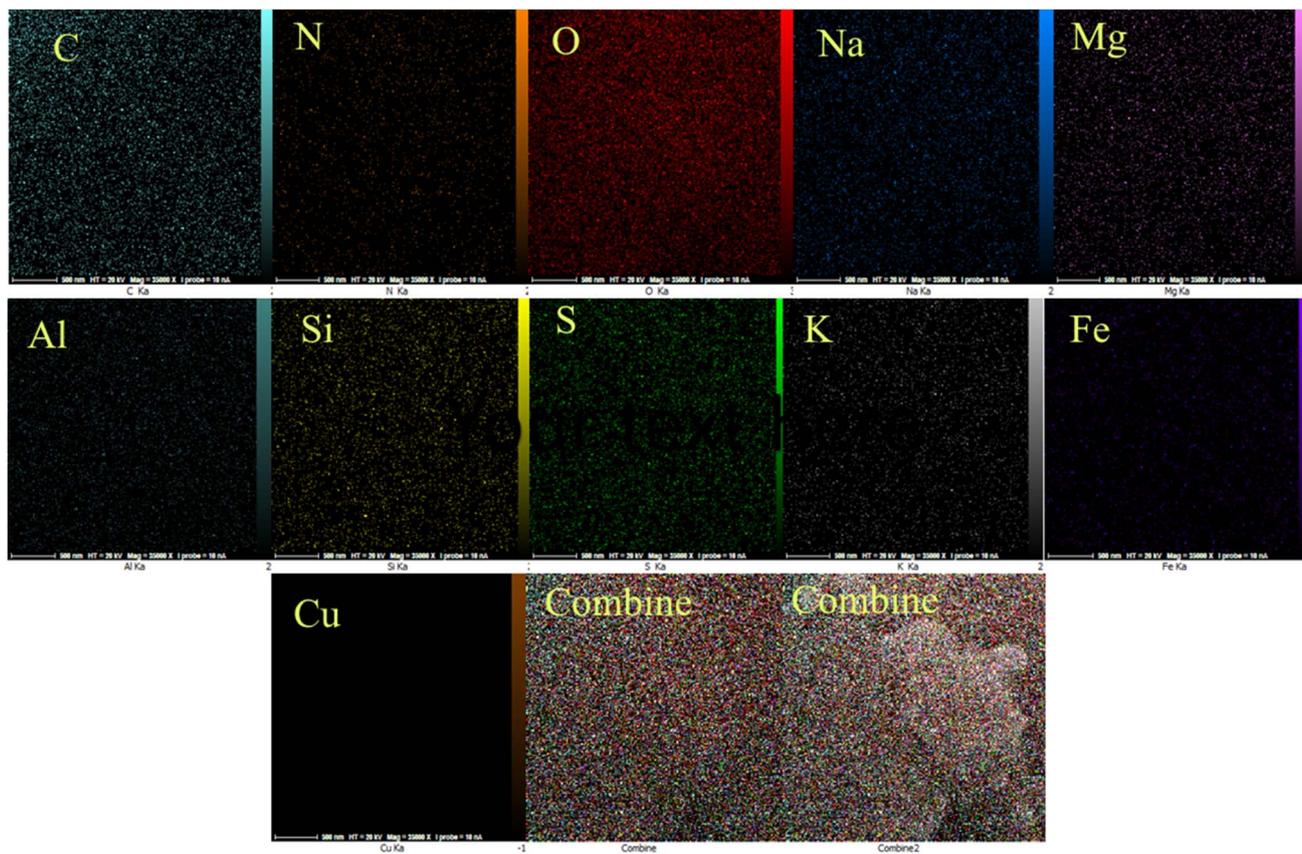


Fig. 8 Elemental mapping of the atoms achieved from the SEM micrographs.

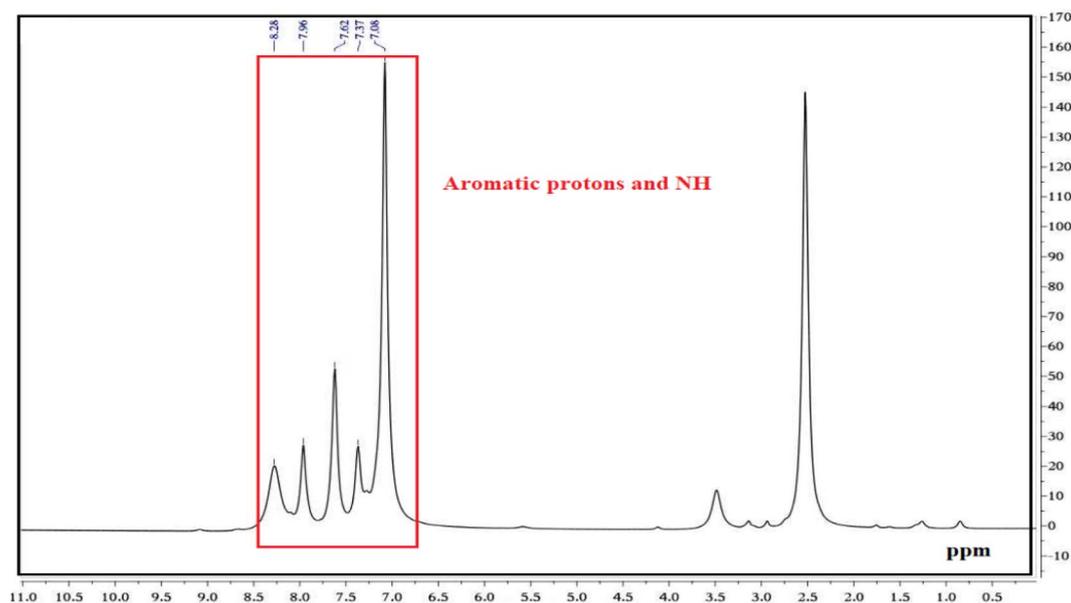


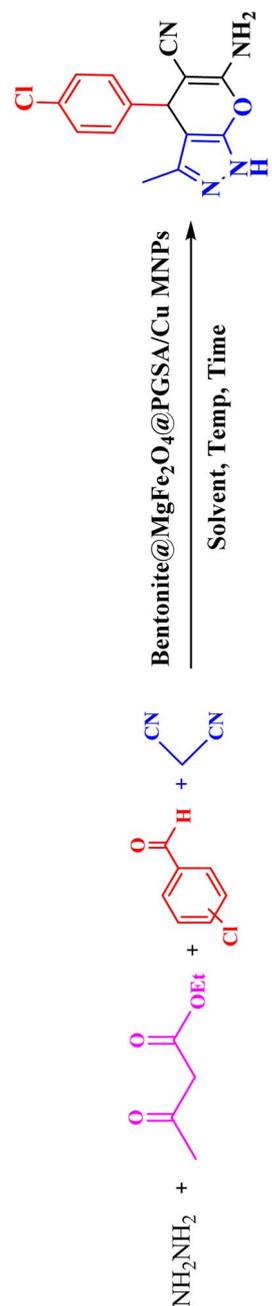
Fig. 9 HNMR of PGSA.

(IV), which undergoes an intramolecular cyclization reaction. Finally, the target products are formed *via* tautomerization (1,3 H shift)^{48,49} (Scheme 3).

The recovery and reusability of the nanomagnetic catalysts were completed to examine the stability and preservation of the catalytic activity. The reaction was done in the presence of the



Table 2 Optimization of reaction conditions



Entry	Cat. (mol%)	Solvent	Time (min)	Yield ^a (%)
1	—	H ₂ O	30	N.R.
2	Bentonite@MgFe ₂ O ₄ @PGSA/Cu (0.2)	DMF	30	80
3	Bentonite@MgFe ₂ O ₄ @PGSA/Cu (0.2)	Toluene	60	68
4	Bentonite@MgFe ₂ O ₄ @PGSA/Cu (0.2)	EtOH	15	90
5	Bentonite@MgFe ₂ O ₄ @PGSA/Cu (0.2)	Solvent-free	30	72
6	Bentonite@MgFe ₂ O ₄ @PGSA/Cu (0.2)	H ₂ O	10	98
7	Bentonite@MgFe ₂ O ₄ @PGSA/Cu (0.1)	H ₂ O	10	73
8	Bentonite@MgFe ₂ O ₄ @PGSA/Cu (0.3)	H ₂ O	10	96
9 ^b	Bentonite@MgFe ₂ O ₄ (0.05 g)	H ₂ O	30	65
10 ^c	PGSA (0.05 g)	H ₂ O	30	55
11 ^d	Bentonite@MgFe ₂ O ₄ @PGSA (0.05 g)	H ₂ O	20	83
12 ^e	Bentonite@MgFe ₂ O ₄ /Cu (0.2)	H ₂ O	30	75

^a Isolated yield. ^b The model reaction was examined in the presence of Bentonite@MgFe₂O₄. ^c The model reaction was examined in the presence of PGSA. ^d The model reaction was examined in the presence of Bentonite@MgFe₂O₄ @PGSA. ^e The model reaction was examined in the presence of Bentonite@MgFe₂O₄/Cu.

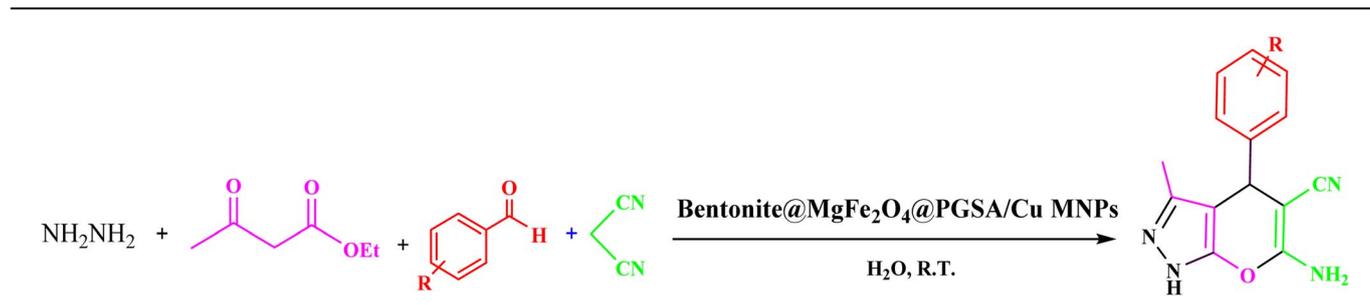


Table 3 Synthesis of pyrano[2,3-c]pyrazoles from different aldehydes using Bentonite@MgFe₂O₄@PGSA/Cu^a

Entry	Substrate	Product	Time (min)	Yield ^b (%)	Melting point (°C)	
					Measured	Literature
1			20	90	262–264	262–264 (ref. 42)
2			20	92	82–83	82–83 (ref. 42)
3			25	90	247–249	247–249 (ref. 43)
4			20	94	240–242	240–242 (ref. 43)



Table 3 (Contd.)



Entry	Substrate	Product	Time (min)	Yield ^b (%)	Melting point (°C)	
					Measured	Literature
5			15	95	97–98	95–97 (ref. 43)
6			10	98	243–245	244–245 (ref. 43)
7			10	95	244–246	244–246 (ref. 43)
8			10	98	258–260	259–261 (ref. 43)
9			10	91	69–70	69–70 (ref. 42)

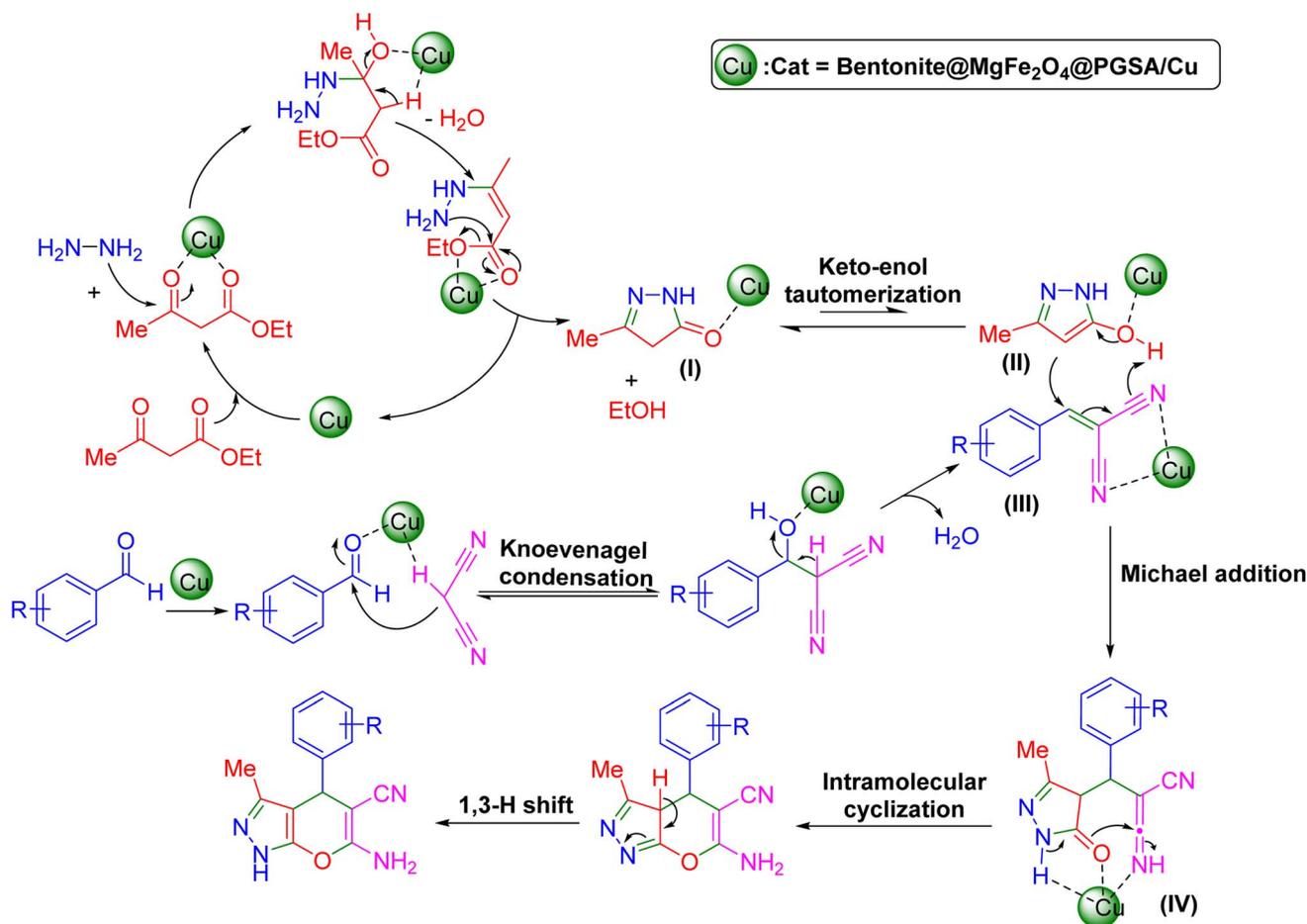


Table 3 (Contd.)

Entry	Substrate	Product	Time (min)	Yield ^b (%)	Melting point (°C)	
					Measured	Literature
10			10	95	211–212	212–213 (ref. 42)
11			10	94	241–243	240–242 (ref. 42)
12			15	93	224–226	226–228 (ref. 43)
13			15	88	220–221	224–225 (ref. 43)

^a Reaction conditions: benzaldehyde derivatives (1 mmol), ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), malononitrile (1 mmol); and Bentonite@MgFe₂O₄@PGSA/Cu (0.2 mol%) were stirred at room temperature. ^b Isolated yield.





Scheme 3 The plausible reaction mechanism of Bentonite@MgFe₂O₄@PGSA/Cu-catalyzed synthesis of pyrano[2,3-c]pyrazoles.

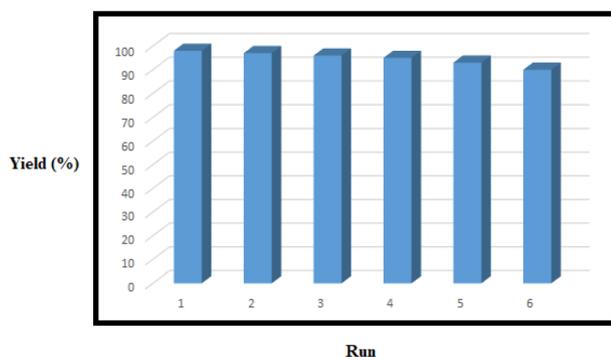


Fig. 10 Recycling of the Bentonite@MgFe₂O₄@PGSA/Cu for the reaction of benzaldehyde, ethyl acetoacetate, hydrazine hydrate, and malononitrile.

six-time recycled Bentonite@MgFe₂O₄@PGSA/Cu without a notable decrease in the activity (Fig. 10). The negligible decrease is due to the catalyst loss during the recycling procedure (the concentration of silver was determined by ICP-AES that changed 1.3% to 1.28% after the 6th run). Therefore, the Bentonite@MgFe₂O₄@PGSA/Cu are highly stable under the studied reaction conditions.

4 Conclusion

In conclusion, the current study found a path to change bentonite to a worthy solid catalyst. The immobilization of copper ion on core-shell Bentonite@MgFe₂O₄@PGSA gives a heterogeneous, green, and recyclable solid acid catalyst for the synthesis of 1,4-dihydropyrano[2,3-c] pyrazole compounds. Furthermore, the prevailing synthesis technique is a type of green, powerful, easy, economical, and environmental strategy to prepare other composites with bentonite and other clay as the support. As a result, bentonite was transformed into a magnetic, green, cheap, and environment-friendly catalyst. The highlights of this work were the mild reaction conditions, the retrievability of the nanocomposite for at least six times, high yields, and environment-friendly profiles with the traditional protocols.

Conflicts of interest

The authors declare no competing interests.

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