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Immobilized PMA on a pyridine-based rigid polymer as a heterogeneous catalyst for the synthesis of 5-aminopyrazole-4-carbonitrile

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Abstract

Phosphomolybdic acid (PMA), characterized by strong Brønsted acidity, redox activity, and thermal stability, is a leading candidate in heterogeneous catalyst design. However, challenges such as leaching and activity loss across multiple cycles limit its practical applications. In this study, immobilizing PMA on a rigid pyridine-based polymeric framework enhances the stability of acidic sites and enables catalyst recyclability. The polymeric support, with appropriate surface area and well-defined porosity, facilitates substrate access to the active PMA sites, thereby improving catalytic efficiency. The resulting catalyst afforded high yields (65–95%) in the synthesis of 5-aminopyrazole-4-carbonitrile in short reaction times (10–90 min). Moreover, the catalyst maintained its activity over at least five consecutive cycles without significant loss. These findings indicate that integrating PMA with rigid polymeric frameworks offers a promising approach to developing heterogeneous catalysts that exhibit high efficiency, structural robustness, and recyclability with considerable potential for acid-catalyzed organic transformations.

Keywords: Phosphomolybdic acid, Rigid polymeric structure, Pyrazole, Heterogeneous catalysis

1. Introduction

Heteropoly acids (HPAs), particularly Keggin-type phosphomolybdic acid (PMA, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$), have attracted significant attention as efficient solid Brønsted acids owing to firm acidity, high redox flexibility, and well-defined molecular structures [1,2]. In the past decade, remarkable progress has been made in designing and functionalizing nanoporous HPAs, leading to substantial improvements in their catalytic activity, stability, and applicability in diverse organic transformations [3,4]. Despite these advantages, pristine PMA suffers from critical drawbacks, including high solubility in polar media, low specific surface area, and limited structural robustness under reaction conditions [5–7]. These intrinsic limitations hinder its direct application as a recoverable heterogeneous catalyst in liquid-phase processes and underscore the need for suitable immobilization strategies [8,9]. To overcome these challenges, incorporating PMA into solid supports with tailored chemical functionalities has proven highly effective [10,11]. Recent studies show that immobilizing HPA clusters on organic frameworks not only enhances their surface accessibility but also mitigates leaching, thereby ensuring long-term catalytic stability [12–14]. Among supports, pyridine-based rigid polymeric frameworks have gained prominence due to their strong Lewis basicity, high cross-linking density, and structural versatility [15,16]. The nitrogen atoms of the pyridine moieties engage in strong coordinative and electrostatic interactions with the PMA anions, thereby forming robust acid–base assemblies within the polymer matrix [17,18]. This confinement effect improves the dispersion of PMA nanoclusters, increases the catalyst’s thermal/mechanical stability, and sustains the integrity of the Keggin structure during repeated catalytic cycles [19,20]. Five-membered heterocycles bearing more than one heteroatom constitute a significant class of bioactive organic compounds, with pyrazoles representing a key subgroup due to the aromatic stabilization provided by their N–N moiety. Pyrazole derivatives and their salts exhibit diverse pharmacological properties, including anti-inflammatory, sedative, hypnotic, antipyretic, antifungal, antibacterial, antibiotic, and antitumor effects—highlighting their broad medicinal potential [21,22]. Their structural adaptability also enables the formation of more complex fused systems, including pyrazoloisoquinolines, pyrazolopyrimidines, pyrazolopyridines, and pyrazolopyrazines [23–25]. A wide variety of synthetic procedures have been reported for constructing pyrazole frameworks. Saleh et al. prepared pyrazolo[3,4-*b*]pyridines from reactions involving a phenylsulfone synthon and *N*-phenyl benzene carbohydrazonyl chloride [26]. Trofimov and co-workers described a stereospecific cyclization of 1,2-acetylene-3-hydroxynitriles with thiosemicarbazide, yielding 3-amino-3-hydroxyalkyl-1-aminothiocarbonyl pyrazoles [27]. Ortiz et al. synthesized new pyrazole derivatives via a solvent-free Diels–Alder reaction of 1,2,3-triazoles with diethyl acetylenedicarboxylate

(DMAD) under pyrolytic conditions [28]. Additional routes include 1,3-dipolar cycloaddition of diazo compounds with alkynes [29], multicomponent reactions of aldehydes, malononitrile, and hydrazines [30], Michael addition of 2-methyl-3-nitrochromene [31], four-component condensations generating oxoalkanenitrile or aminonitrile substrates [32], and reactions of enamines with hydroxylamine hydrochloride [33].

Recent advances in pyrazole synthesis have increasingly moved toward environmentally benign methodologies. Green chemistry strategies promote mild, safe solvents such as water and ethanol, solvent-free conditions, low-cost, abundant catalysts, and one-pot, multicomponent systems. Nanostructured and polymer-supported catalysts are particularly valuable because their high surface area enhances accessibility to active sites, improves activity and selectivity while minimizing byproduct formation. Furthermore, their heterogeneous nature allows simple recovery and reuse, making them attractive candidates for sustainable synthesis [33–37].

The synergistic integration of Brønsted-acidic PMA with the Lewis-basic pyridine framework generates a multifunctional catalytic environment that promotes a wide range of reactions, particularly those requiring the activation of both electrophilic and nucleophilic intermediates. Such features make the PMA polymer hybrid particularly well-suited for multicomponent and condensation pathways, including the synthesis of nitrogen-containing heterocycles. In this context, the catalytic formation of 5-aminopyrazole-4-carbonitrile serves as an excellent model reaction for evaluating the performance of the immobilized PMA system. The rigid pyridine-based polymer not only stabilizes heteropoly anions via acid–base interactions but also enhances substrate orientation and intermediate stabilization, ultimately improving reaction efficiency, selectivity, and recyclability.

2. Experimental

2.1. Materials and Methods

All reagents were obtained from Sigma-Aldrich and used as received, without further purification. Fourier-transform infrared spectroscopy measurements were conducted using a Shimadzu IR Prestige-21 instrument. Melting point determinations for synthesized materials were performed with a Barnstead Electrothermal IA9200 device. Nuclear magnetic resonance spectra were acquired on a Bruker DRX-500 Avance system operating at 500 MHz for ^1H nuclei and 125 MHz for ^{13}C nuclei, using DMSO- d_6 as a solvent. A PANalytical X'Pert Pro

diffraction system was used to investigate the crystalline characteristics of particles. Surface topology and elemental analysis were examined via scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDS) using a TESCAN MIRA3 apparatus. Thermal degradation behavior was evaluated through thermogravimetric analysis employing an SDT Q600 V20.9 Build 20 system under atmospheric conditions, spanning 25-800 °C at a 10 °C/min heating rate. The surface area and porosity characteristics were determined using a TriStar II PLUS analyzer.

2.2. Preparation of TA-DAP@PMA

TA-DAP was synthesized following a previously reported method [38]. Following this, 1 g of TA-DAP was dispersed in 50 mL of EtOH and ultrasonicated for 20 min. Subsequently, 0.01 g of phosphomolybdic acid was added, and the mixture was ultrasonicated for 15 min, then stirred at ambient temperature for 12 h. After completion, the product was isolated through centrifugation and thermally treated at 150 °C for 15 h.

2.3. Synthesis of 5-aminopyrazole-4-carbonitrile with the TA-DAP@PMA catalyst

A round-bottom flask (50 mL) was filled with 20 mL of a 50% v/v ethanol-distilled water mixture. Then, malononitrile (1 mmol) and TA-DAP@PMA (0.1 mmol) were added to the solution, and the mixture was magnetically stirred. Subsequently, substituted benzaldehyde (1 mmol) was added to the stirring mixture, and agitation continued for 3 min until light precipitation appeared. Thereafter, substituted phenylhydrazine (1 mmol) was added, resulting in dense precipitation. Stirring at ambient temperature continued until the reaction was complete, monitored by thin-layer chromatography. The final product was collected by filtration, washed with water, oven-dried, and purified by column chromatography using n-hexane: ethyl acetate as the eluent.

2.4. Spectral data for selected compounds

5-Amino-1,3-diphenyl-1H-pyrazole-4-carbonitrile (5a): White solid [39]; ¹H NMR (301 MHz, DMSO-*d*₆) δ 7.92 (s, 2H), 7.68 (m, 2H), 7.56 – 7.19 (m, 5H), 7.18 – 7.02 (m, 2H), 6.89 – 6.49 (m, 1H); ¹³C NMR (76 MHz, DMSO-*d*₆) δ 148.83, 145.27, 138.38, 134.27, 132.01, 130.64, 129.71, 122.45, 120.00, 119.95, 112.80.

5-Amino-3-(3-nitrophenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (5c): White solid [40]; ¹H NMR (301 MHz, DMSO-*d*₆) δ 8.49 (s, 1H), 8.25 – 8.03 (m, 2H), 8.02 (s, 2H), 7.85 – 7.54 (m, 1H),

7.37 – 7.18 (m, 2H), 7.16 (d, $J = 7.6$ Hz, 2H), 6.84 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR (76 MHz, DMSO- d_6) δ 145.46, 138.69, 136.64, 135.08, 134.05, 131.00, 129.66, 127.91, 125.29, 124.72, 119.65, 112.68.

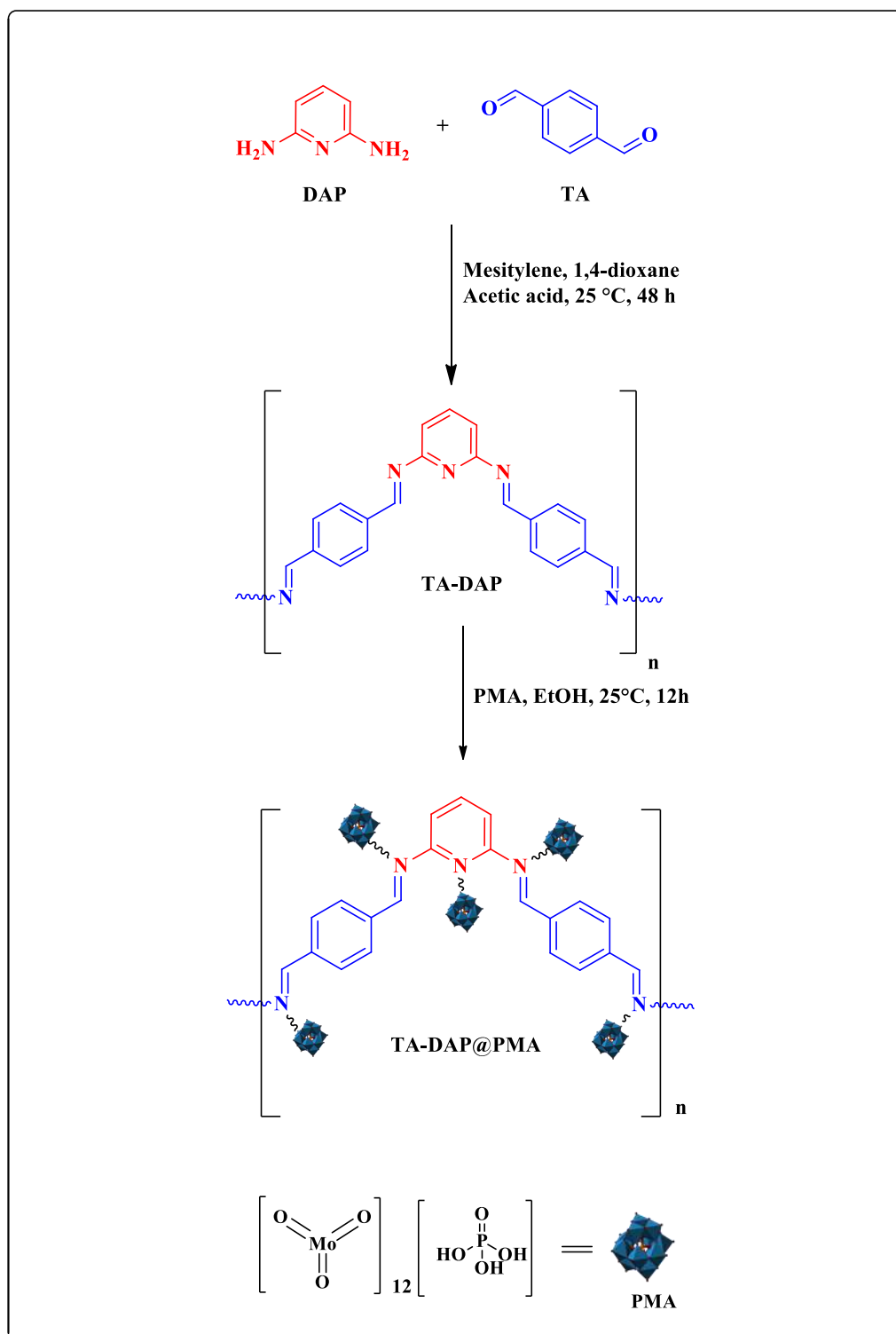
5-Amino-3-(4-chlorophenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (5g): White solid [41]; ^1H NMR (301 MHz, DMSO- d_6) δ 7.89 (d, $J = 19.8$ Hz, 1H), 7.73 (d, $J = 1.7$ Hz, 1H), 7.60 (s, 2H), 7.50 – 7.17 (m, 4H), 7.14 (d, $J = 10.0$ Hz, 2H), 6.90 – 6.60 (m, 1H); ^{13}C NMR (76 MHz, DMSO- d_6) δ 145.53, 141.45, 132.52, 129.64, 128.09, 127.07, 126.24, 119.28, 112.38.

5-Amino-3-(4-chlorophenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (5i): White solid [42]; ^1H NMR (301 MHz, DMSO- d_6) δ 8.09 (s, 1H), 7.47 (s, 1H), 7.32 – 7.14 (m, 3H), 7.12 – 7.04 (m, 1H), 7.02 (dd, $J = 12.5, 6.3$ Hz, 2H), 6.81 – 6.63 (m, 1H); ^{13}C NMR (76 MHz, DMSO- d_6) δ 145.80, 136.93, 136.34, 129.62, 129.15, 128.42, 126.12, 119.25, 112.49.

3. Results and discussion

3.1. Characterization of TA-DAP as a heterogeneous catalyst

The preparation protocol for TA-DAP is illustrated in Scheme 1. The resulting material underwent comprehensive characterization employing multiple analytical methods, including FT-IR, XRD, FE-SEM, TGA, and BET surface measurements.



Scheme 1. TA-DAP@PMA synthesis.

FT-IR spectra (Fig. 1) reveal characteristic bands for TA-DAP and TA-DAP@PMA. For TA-DAP (Fig. 1a), N–H stretching is observed at 3300–3500 cm^{-1} , C=N stretching at 1600–1650 cm^{-1} , aromatic C=C stretching at 1450–1500 cm^{-1} [39]. After PMA loading (Fig. 1b), the 3600–3000 cm^{-1} band broadens and intensifies, indicating hydrogen bond formation with crystal

water. A slight shift in the C=N band suggests protonation of the pyridine nitrogen. New bands at 1060, 960, 870, and 780 cm^{-1} confirm the presence of intact PMA Keggin units via P–O, terminal Mo=O, and Mo–O–Mo vibrations. Unchanged aromatic C=C stretching bands indicate preservation of the polymer backbone. These results confirm that PMA is stabilized on TA-DAP via $\text{Py-N}\cdots\text{H-O-Mo}$ hydrogen bonding, thereby ensuring uniform dispersion, structural stability, and acidic site accessibility. Negligible spectral changes in recycled samples demonstrate the hybrid material's robustness.

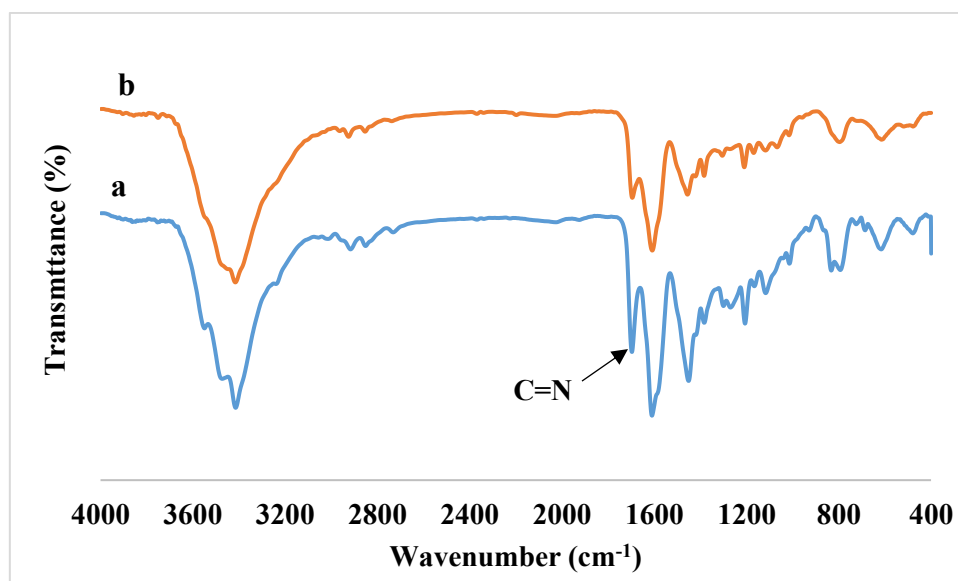


Fig. 1. FT-IR spectra of (a) TA-DAP, (b) fresh TA-DAP@PMA and (c) reused TA-DAP@PMA.

FESEM analysis revealed a uniformly spherical morphology characteristic of the imine-linked polymeric structure. TA-DAP showed some degree of aggregation, as shown in Fig. 2a, b, with measured aggregate dimensions averaging 1.3 μm (Fig. 2e) [39]. During the PAM stabilization procedure, TA-DAP maintained its structural stability (Fig. 2c, d), and the average aggregate size was 0.55 μm (Fig. 2f). EDX analysis indicated the presence of C and N in TA-DAP and C, N, O, and Mo in TA-DAP@PMA. Elemental mapping (Fig. 3) demonstrated a homogeneous element distribution.

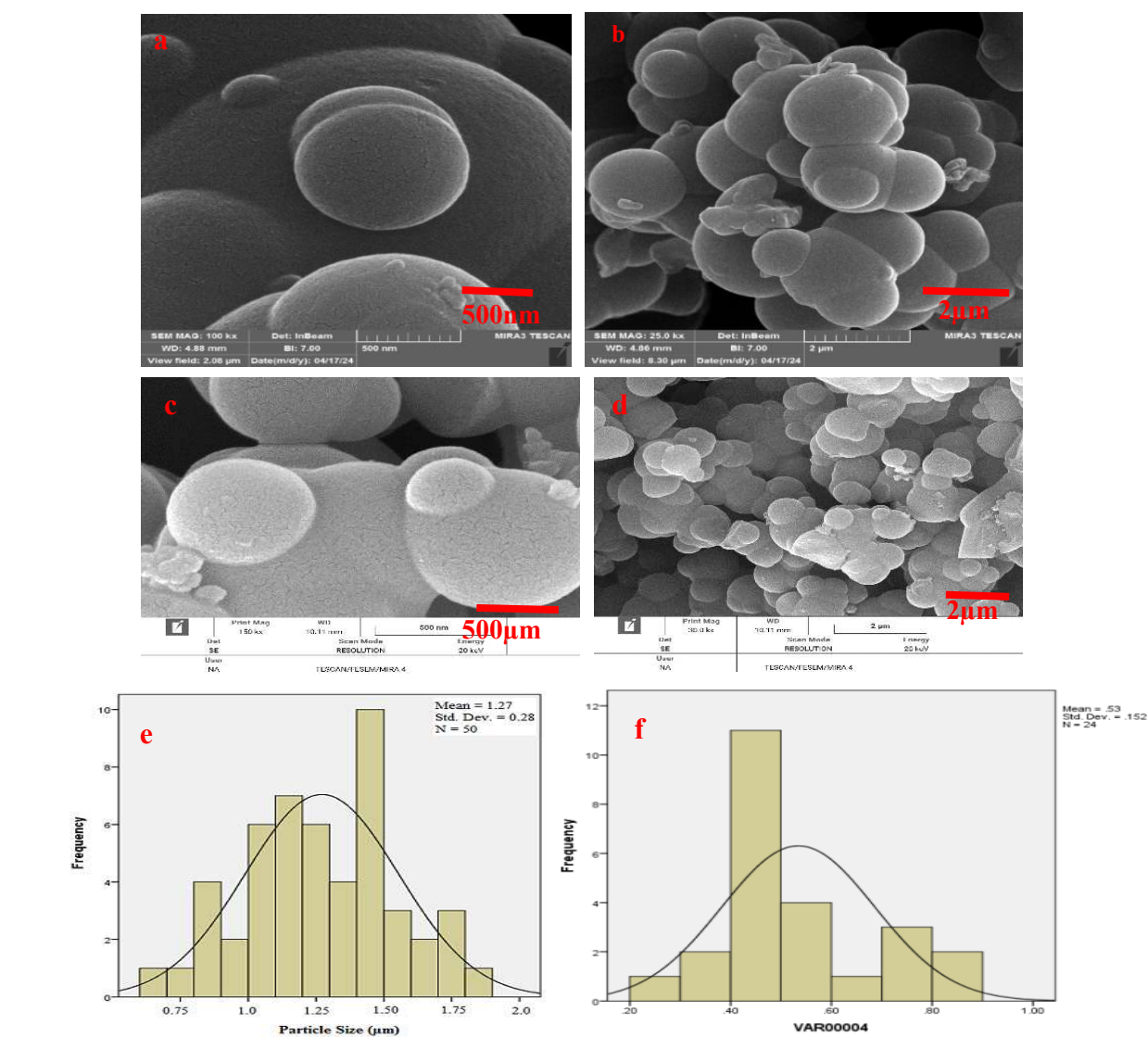


Fig. 2. FESEM images of TA-DAP (a,b), TA-DAP@PMA (c, d), and particle size distribution of TA-DAP (e) and TA-DAP@PMA (f).

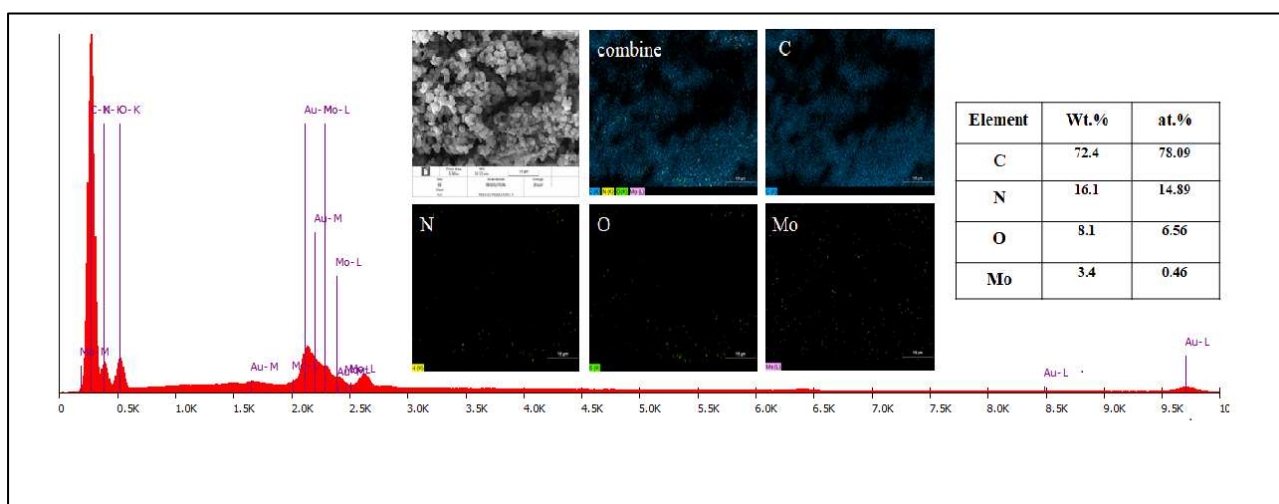
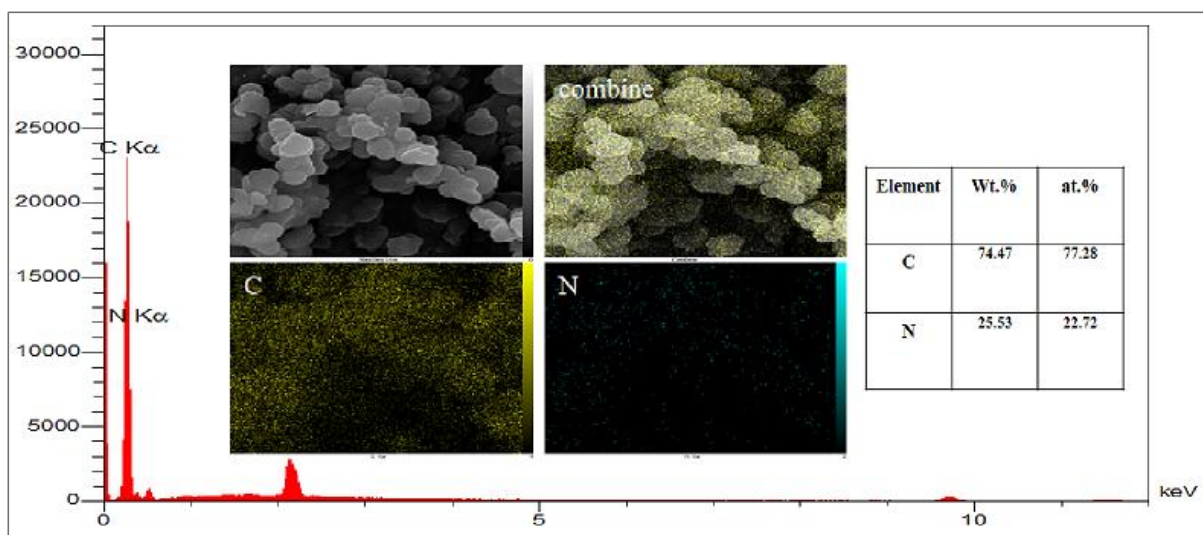


Fig.3. EDX spectra and related elemental-mapping images of TA-DAP and TA-DAP@PMA.

X-ray diffraction patterns of TA-DAP and TA-DAP@PMA are presented in Fig. 4. TA-DAP exhibited limited crystallinity, showing a broad diffraction feature at $2\theta \approx 21.5^\circ$, characteristic of amorphous character and π - π stacking in the two-dimensional layered architecture [39]. After PMA immobilization, the intensity of diffraction peaks increased, and sharp reflections appeared between $2\theta \approx 10^\circ$ and 30° , indicating a more ordered crystalline structure. These results suggest that the Keggin-type PMA enhanced the composite's overall crystallinity, confirming successful PMA loading and stabilization on the TA-DAP support. Furthermore, a slight shift toward lower 2θ angles was noted due to increased d-spacing in TA-DAP.

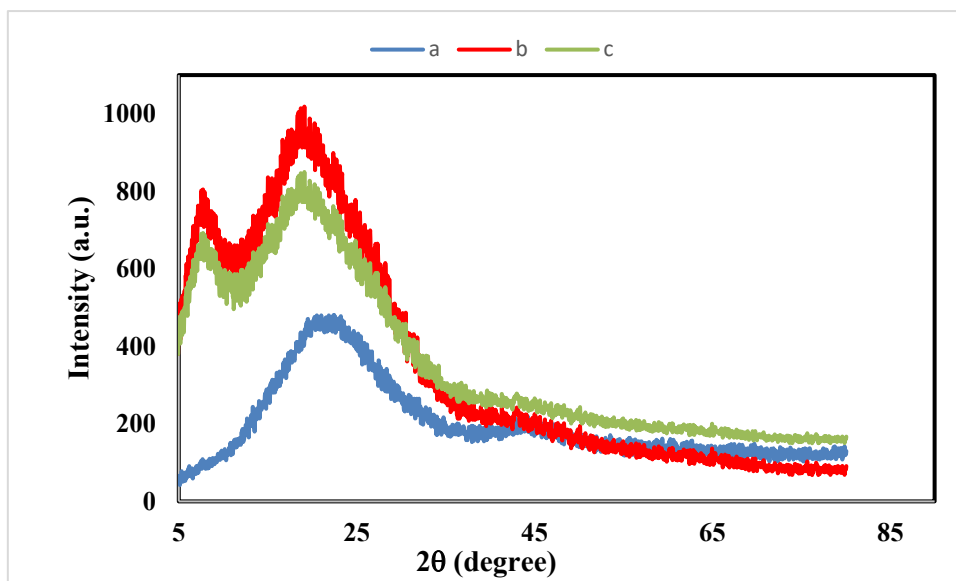


Fig.4. XRD pattern of (a) TA-DAP, (b) fresh TA-DAP@PMA, and (C) reused TA-DAP@PMA.

TGA analysis was performed in the temperature range of 40-800 °C to evaluate the thermal stability of TA-DAP (a) and TA-DAP@PMA (b) (Fig. 5). The TA-DAP exhibited three distinct degradation stages: (i) initial weight loss (~10%) below 200 °C attributed to moisture and solvent evaporation, (ii) gradual decomposition (200-500 °C) corresponding to polymer chain degradation, and (iii) rapid thermal decomposition (500-800 °C) resulting in 40% residual mass at 800 °C due to carbonization (39). TA-DAP@PMA demonstrated superior thermal stability with approximately 65% residual mass at 800 °C. The decomposition profile showed initial dehydration (~10% weight loss) below 300 °C, followed by progressive degradation of the heteropolyacid structure (300-650 °C), ultimately forming stable molybdenum and phosphorus oxide residues. The higher thermal stability of TA-DAP@PMA compared to TA-DAP is attributed to its robust inorganic framework, making it suitable for high-temperature catalytic and composite applications.

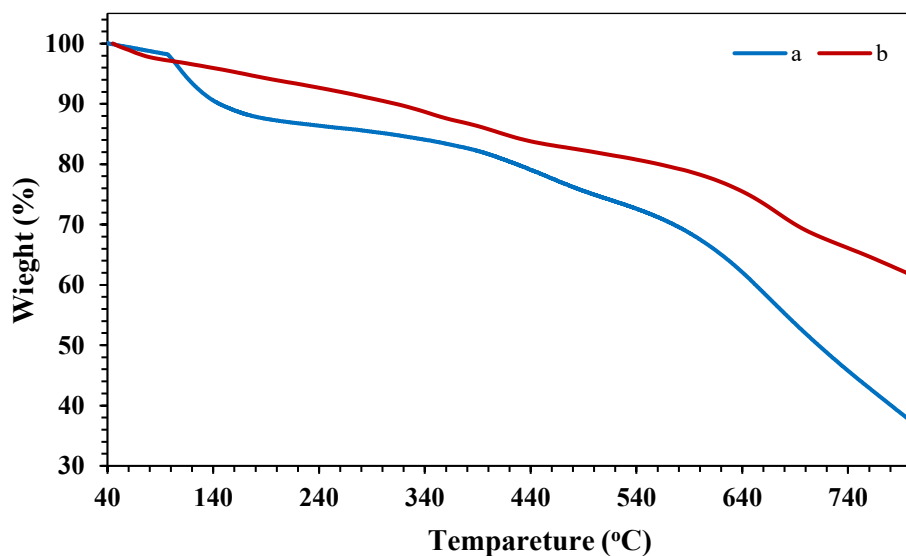


Fig.5. Thermogravimetric analysis (TGA) of TA-DAP and TA-DAP@PMA.

Based on Fig. 6 and Table 1, Nitrogen adsorption-desorption isotherm measurements were performed to assess porous characteristics. Pure TA-DAP polymer exhibited a type IV isotherm with H3 hysteresis, indicating a mesoporous architecture with slit-shaped pores (39). After phosphomolybdic acid immobilization, TA-DAP@PMA composite exhibited a more distinct type IV isotherm with H2 hysteresis, implying formation of more intricate mesopores with bottle-neck geometries. BET analysis indicated that accessible surface area declined from 15 to 12 m²/g, total pore volume decreased from 0.0179 to 0.0093 cm³/g, and mean pore diameter reduced from 7.08 to 2.63 nm upon PMA integration. These modifications indicate partial pore occupation by PMA molecules within the polymer matrix. Despite these reductions in textural parameters, the overall mesoporous architecture remained intact, confirming successful PMA immobilization and homogeneous distribution throughout the polymer framework while preserving mesoporous accessibility.

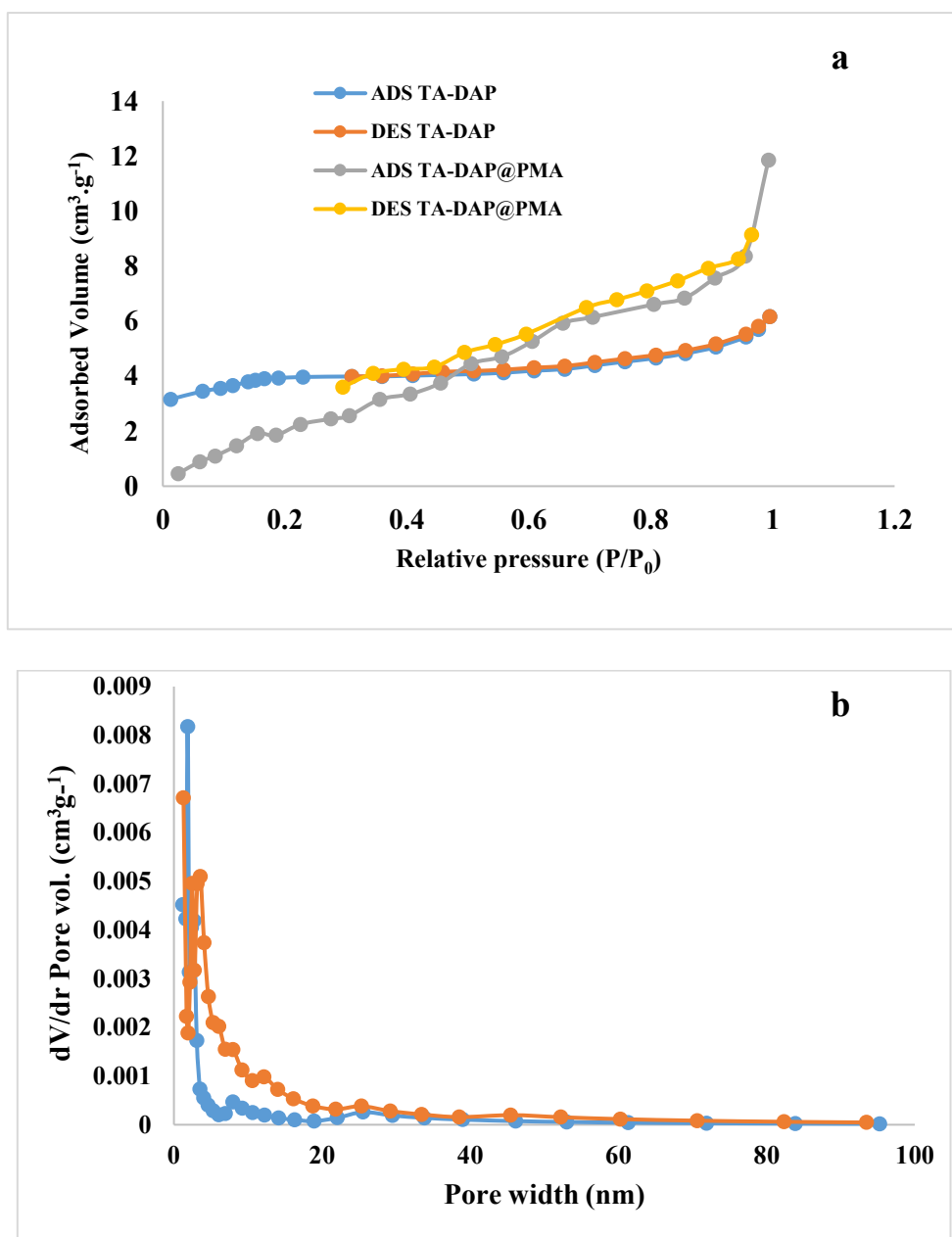


Fig. 6. (a) N₂ adsorption-desorption isotherms and (b) pore size distribution curves of TA-DAP and TA-DAP@PMA.

Table 1. The BET surface area and the porosity data for TA-DAP and TA-DAP@PMA.

Materials	Specific surface area (m ² g ⁻¹) ^a	Total pore volume (cm ³ g ⁻¹) ^b	Mean pore size (nm) ^c
TA-DAP	15	0.017905	7.0777
TA-DAP@PMA.	12	0.0093387	2.6295

^a SBET

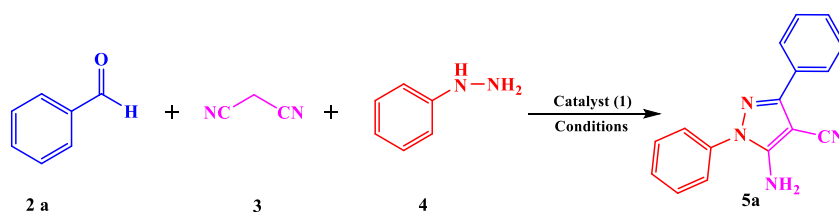
^b Total pore volume determined at $P/P^0 = 0.99$

^c Mean pore diameter determined using the BJH model

3.2. Catalysis of 5-aminopyrazole-4-carbonitrile by TA-DAP@PMA

Evaluating TA-DAP@PMA catalytic activity constituted a primary objective of this research. Initially, the condensation of benzaldehyde (2a, 1 mmol), malononitrile (1 mmol, 3), and phenylhydrazine (1 mmol, 4) was selected for optimization regarding catalyst amount, reaction medium, and temperature. The model reaction produced no products in the absence of the catalyst (Table 2, entry 1). Subsequently, solvent optimization was performed using different solvents, such as methanol, acetonitrile, ethyl acetate, ethanol, water, and an ethanol: water combination (1:1). The results clearly demonstrated that an ethanol: water (1:1) mixture provided a superior outcome (Table 2, entries 2-8). We explored temperatures from ambient to 100 °C, tested catalyst loadings from 0.01 to 0.45 g (Table 2, entries 10-16), and evaluated the effect of reaction duration by conducting experiments at 10 and 30 min (Table 2, entries 17 and 18). The results indicated that an extended reaction period has minimal impact on product yield (Table 2, entry 17), while shortened reaction times reduced yields (Table 2, entry 18). Consequently, optimal yield (95%) and the shortest reaction time (15 min) were achieved using 0.04 g of the TA-DAP@PMA catalyst at 55 °C in a water/ethanol solvent system (Table 2, entry 15).

Table 2. The optimization of the reaction. ^a



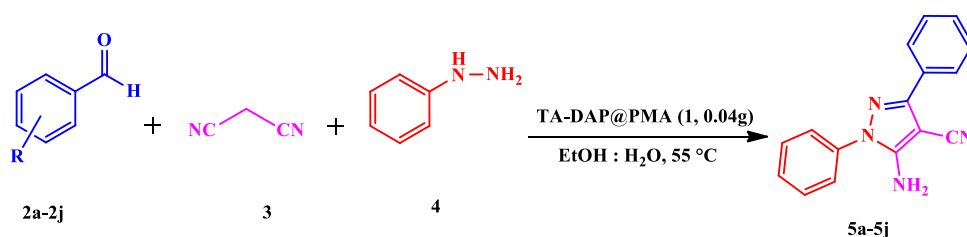
Entry	Catalyst	Catalyst amount (g)	Solvent	Temp. (°C)	Time (min)	Yield (%) ^b
1	TA-DAP@PMA	-	EtOH: H ₂ O	100	180	Trace ^c
2	TA-DAP@PMA	0.04	MeOH	Reflux	15	35
3	TA-DAP@PMA	0.04	CH ₃ CN	Reflux	15	25
4	TA-DAP@PMA	0.04	EtOAc	Reflux	15	30

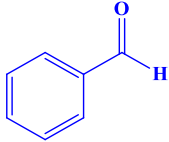
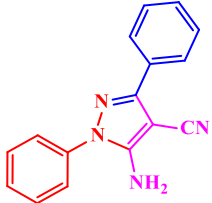
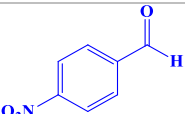
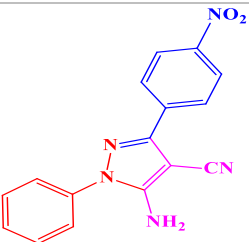
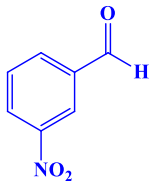
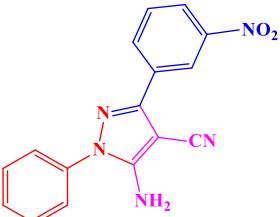
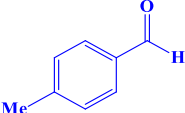
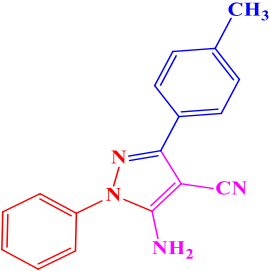
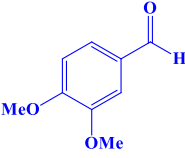
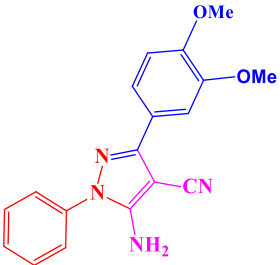
5	TA-DAP@PMA	0.04	EtOH	Reflux	15	40
6	TA-DAP@PMA	0.04	H ₂ O	Reflux	15	Trace
7	TA-DAP@PMA	0.04	EtOH: H ₂ O	Reflux	15	94
8	TA-DAP@PMA	0.04	EtOH: H ₂ O (1:1)	70	12	94
9	TA-DAP@PMA	0.04	EtOH: H ₂ O (1:1)	60	15	94
10	TA-DAP@PMA	0.01	EtOH: H ₂ O (1:1)	55	15	70
11	TA-DAP@PMA	0.02	EtOH: H ₂ O (1:1)	55	15	77
12	TA-DAP@PMA	0.025	EtOH: H ₂ O (1:1)	55	15	80
13	TA-DAP@PMA	0.03	EtOH: H ₂ O (1:1)	55	15	88
14	TA-DAP@PMA	0.035	EtOH: H ₂ O (1:1)	55	15	92
15	TA-DAP@PMA	0.04	EtOH: H ₂ O (1:1)	55	15	95
16	TA-DAP@PMA	0.045	EtOH: H ₂ O (1:1)	55	15	95
17	TA-DAP@PMA	0.04	EtOH: H ₂ O (1:1)	55	30	95
18	TA-DAP@PMA	0.04	EtOH: H ₂ O (1:1)	55	10	89

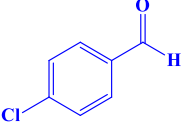
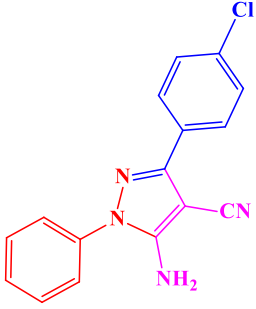
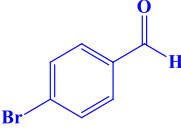
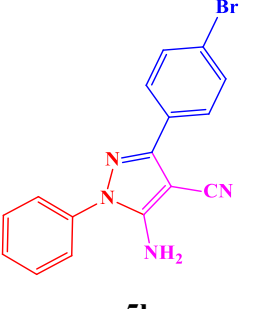
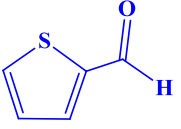
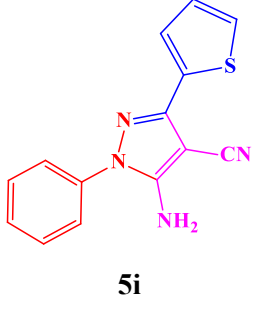
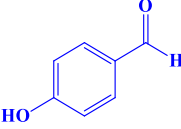
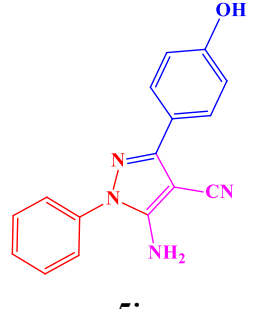
^a Reaction conditions: benzaldehyde (1 mmol), phenylhydrazine (1 mmol), malononitrile (1mmol), and solvent (2 mL). ^b Isolated yield. ^c After 180 min, **5a** wasn't formed.

After optimizing the reaction, we studied the substrate scope using malononitrile, phenylhydrazine, and different aldehydes, including both electron-donating and electron-withdrawing substituents. We obtained the corresponding products in 68-95% yields within 15-45 min (Table 3). Aldehydes bearing electron-withdrawing groups typically showed higher yields and shorter reaction times, attributable to increased electrophilicity of the carbonyl carbon, which promotes nucleophilic attack by phenylhydrazine. Conversely, aldehydes with electron-donating substituents exhibited weaker electrophilic centers, resulting in longer reaction times and lower yields. Furthermore, para-substituted aldehydes afforded excellent yields compared with ortho-substituted counterparts due to reduction of steric interference. Significantly, no side products were observed in any reactions, establishing the methodology's efficiency and selectivity.

Table 3. 5-Aminopyrazole-4-carbonitriles synthesis from phenylhydrazine, malononitrile, and aldehydes. ^a



Entry	Aldehyde	Product	Time (min)	Yield ^b (%)	M.p (°C)
					Found / Reported [Ref]
1	 4a	 5a	15	95	160-162 (159-161) [39]
2	 4b	 5b	15	92	163-165 (162-164) [43]
3	 4c	 5c	17	90	127-129 (128-130) [40]
4	 4d	 5d	25	80	117-119 (118-120) [44]
5	 4e	 5e	45	68	122-125 (124-126) [45]

6	 4g	 5g	15	91	127-129 (128–130) [41]
7	 4h	 5h	15	89	164-165 (163-165) [46]
8	 4i	 5i	17	85	141-144 (143-145) [42]
9	 4j	 5j	30	70	207-209 (208-210) [47]

^a Reaction conditions: aldehydes (**2a-2j**, 1 mmol), malononitrile (**3**, 1 mmol), phenylhydrazine (**4**, 1 mmol), the catalyst (**1**, 0.04 g), 55 °C, solvent (EtOH: H₂O).

^b Isolated yields.

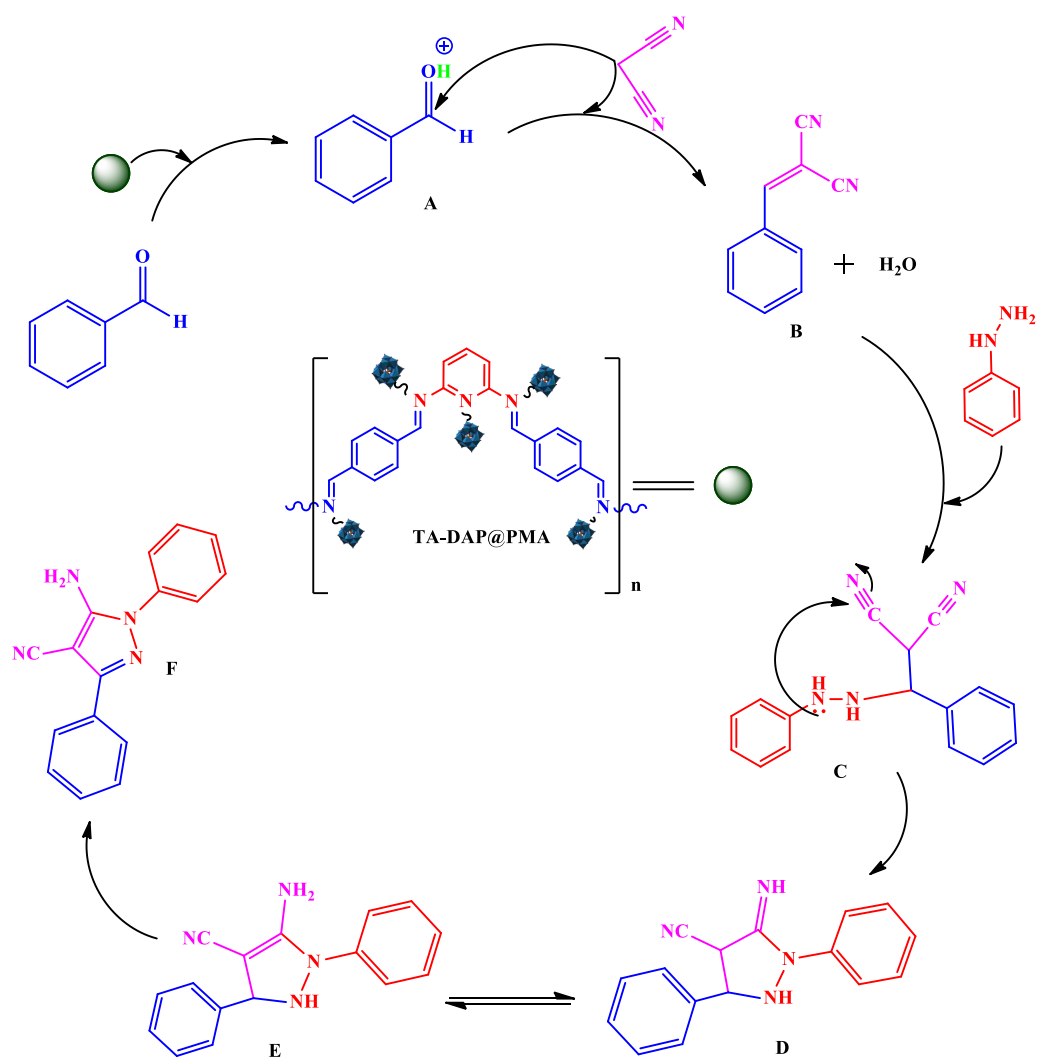
Subsequently, the results of this study were benchmarked against previously reported methodologies to clearly underscore its advantages (Table 4). The comparative analysis reveals that the newly developed catalyst exhibits superior performance across several critical parameters, including reaction time, temperature, and product yield. Notably, the TA-

DAP@PMA catalyst delivers higher yields under milder reaction conditions, thereby markedly improving the overall efficiency of the synthetic process.

Table 4. A comparative study with other catalysts.

Entry	Catalyst	Solvent/T (°C)	Time (min)	Yield (%)	Ref
1	Fe ₃ O ₄ @Alg@CPTMS@Arg	EtOH / reflux	9	86	[48]
2	Fe ₃ O ₄ @CQD@Si(OEt)(CH ₂) ₃ NH@CC@Ad@Cu(OAc)	S. F /30	8	58	[49]
3	CuO/ZrO ₂	H ₂ O /40	90	89	[50]
4	[4CSPy]ZnCl ₃	solvent-free / 80	120	90	[51]
5	LDH@PTRMS@DCMBA@CuI	H ₂ O/EtOH (1:1)/ 55	15	93	[36]
6	AlCl ₃	EtOH: H ₂ O / 80	30	83	[52]
7	TA-DAP@PMA	H ₂ O/EtOH (1:1)/55	15	95	This work

The synthesis mechanism for 5-aminopyrazole-4-carbonitrile derivatives using TA-DAP@PMA catalyst is depicted in Scheme 2. Initially, the catalyst activates the aldehyde by protonating its carbonyl group. Subsequently, malononitrile undergoes Knoevenagel condensation with intermediate A, forming intermediate B. Next, the phenylhydrazine Michael addition occurs, followed by cyclization to produce intermediate E. Finally, enol-keto tautomerization, water elimination, and nanocatalyst separation generate the target product F.



Scheme 2. The proposed mechanism of reactions.

3.3. The reusability and stability of the TA-DAP@PMA

Recovery and repeated use of heterogeneous catalysts are crucial considerations that determine their practical viability in industrial applications. To evaluate durability, TA-DAP@PMA served as an acid organocatalyst in the synthesis of compound 5a. The catalyst could be recycled over five consecutive runs while maintaining essentially consistent catalytic performance (Fig. 7). Post-reaction structural integrity was assessed by FT-IR and XRD analyses after five reuse cycles. Corresponding FT-IR (Fig. 1c) and XRD (Fig. 4c) profiles of recovered catalyst confirmed excellent structural stability.

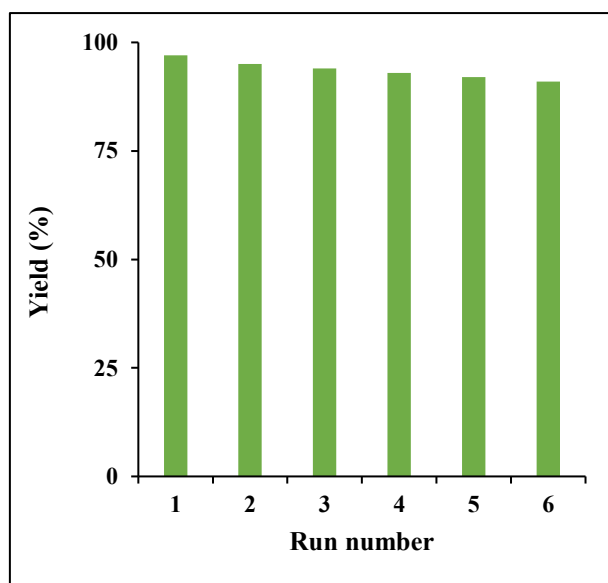


Fig. 7. The recyclability of TA-DAP@PMA for the model substrate (**5a**).

4. Conclusion

In this study, phosphomolybdic acid (PMA) was immobilized in a rigid pyridine-based polymeric framework, resulting in a stable and efficient heterogeneous catalyst. The enhanced structural robustness of the support matrix and the improved accessibility of acidic functional groups enabled the formation of 5-aminopyrazole-4-carbonitrile in high yields with short reaction times. Furthermore, the catalyst demonstrated satisfactory recyclability over five consecutive cycles, with minimal loss of activity. These findings validate the integration of PMA with rigid polymeric supports as a promising approach to designing durable, highly active catalysts for diverse acid-catalyzed organic transformations.

CRediT authorship contribution statement

Sara Saki: Synthesis, Characterization of compounds, writing- investigation.

Mohammad Mehdi Khodaei: Supervision, writing–review & editing, Management and coordination responsibility for the research activity planning and execution.

Declaration of competing interests

We declare that there are no competing financial interests or personal relationships that could affect this paper.

Data availability

Data will be made available on request.

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