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Silica supported phosphotungstic acid catalyzed one pot efficient synthesis of pyrazolopyranopyrimidine derivatives"

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ABSTRACT

A simple highly efficient method for synthesis of pyrazolopyranopyrimidine derivative has been developed. We have prepared heterogeneous silica supported phosphotungstic acid catalyst and characterized completely by different spectroscopic and analytical techniques. After successful characterization of catalyst, it was employed in the synthesis of pyrazolopyranopyrimidine derivatives from barbituric acid, 3-methyl-5-pyrazolone and substituted aryl aldehydes under optimized reaction conditions. Results showed that, silica supported phosphotungstic acid catalyst much more effective and selective catalyst for the synthesis of pyrazolopyranopyrimidine derivatives under greener conditions. Key advantage of this method was easy work up, recyclability of catalyst up to five cycles, highly efficient synthesis of eleven derivatives of pyrazolopyranopyrimidines with 96–88 % isolated yield with maximum purity.

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1. Introduction

Multi-component reactions involve more than two reactants that combine in the proper way to form a single product that contains the essential part of the reactants [1]. A multicomponent reaction is a powerful tool in synthetic organic chemistry and drug design processes, because of its molecular diversity, allowing the rapid and automated generation of organic compounds [2]. Knovengel reaction is the most important route for the construction of the C—C bond in modern organic chemistry [1–3]. Knovengel product usually undergoes Michael-type addition reactions [4]. Several multi-component strategies involving Knovengel condensation and Michael addition followed by intramolecular cyclization have been reported for the synthesis of new fused heterocycles [4–6]. Heterocyclic compounds containing pyrimidine, pyrazole and pyran together has found to possess various pharmacological activities [7]. The pyrimidine nucleus is the core unit of many pharmacological agents which exhibits a broad spectrum of biological properties [7,8]. Furthermore, Pyrazole is another important structural motif that plays a vital role in many pharmaceutical and agrochemical industries [9,10]. The pyran skeleton is the most important structural unit in bioactive compounds, a number of natural products, photochromic and luminescence materials [11,12]. The more prominent effect is observed when two or more heterocyclic units are present in a single molecule. The pyranopyrazole moiety signifies a fascinating template in the pharmaceutical field and shows a wide range of biological activities such as antidepressant, [13] insecticidal [14], hypotensive [15], and anticancer. [16] In contrast, the pyranopyrimidine scaffold as a key member of the pyrimidine family has gained considerable attention due to its wide range of antitumors [17] and prominent antimicrobial & antitubercular activities. [18] Significant biological activity of pyranopyrimidine is due to their occurrence in the structures of various natural products [19]. Fused heterocycle consisting of both Pyranopyrazole & Pyranopyrimidine moieties fascinates probing possible cumulative biological properties. Recently, considerable attention has been given to design strategies leading to structurally diverse and complex molecules.

Heteropolyacid plays an important role in the catalytic system which possesses both Bronsted acidity and redox potentiality

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[20–22]. Different HPAs (Heteropoly acids) are used for catalyzing numerous photochemical, organic [23–26], electrochemical [27], and petrochemical [28] reactions. Although all the interesting features of HPAs such as their non-corrosive and nontoxic nature, are sensitive to light and electricity, they suffer from some drawbacks like low surface area and high water solubility and conventional organic solvents. Recently, heterogeneous catalysis attracted the researcher's attention due to its basic characteristic of easy separation. Supported Heteropolyacid have more important applications due to it have high specific area with more acidic sites on the surface compared to Heteropolyacid [29]. So, it is necessary to find out appropriate support to increase specific areas of phosphotungstic acid. Silica- supported phosphotungstic acid was utilized in different reactions like α-pinene polymerization [30], β-pinene polymerization [31] and many others.

The most common method for synthesis of pyrazolopyranopyrimidinedione derivatives is condensation reaction between pyrazoline, aromatic aldehyde and barbituric acid in presence of various catalyst such as, Meglumine [32], SBA-Pr-SO_3H as a Nanoporous acid catalyst [33], Nano Fe_2O_3 supported organocatalyst [34]. Reported literature suffers from a few limitations such as long reaction time, low yield, the requirement of excess and toxic reagent and tedious work-up procedure therefore, there is need to develop highly efficient catalytic system in the synthesis of Pyrazolopyranopyrimidinedione.

In continuation of our research work on the development of constructive methodologies, we reported highly efficient environment pleasant, silica supported phosphotungustic acid as catalyst for synthesis of Pyrazolopyranopyrimidines derivatives. In addition detail, the synthesis and characterization of synthesized catalyst were obtained and structural confirmation has been done. In addition, optimization of reaction conditions was studied in detail and the same has been discussed. Recyclability of catalyst and number of substituted derivatives were prepared in good to efficient yield.

2. Materials and methods

2.1. Materials

All the chemicals including Phosphotungstic acid (99.0 %), aryl aldehydes (99.0 %), Pyrazoline (99.0 %) fumed silica & barbituric acid (99.0 %) were purchased from Sigma Aldrich and used directly without further purification.

2.2. Catalyst preparation

Fumed silica was treated with 1 M hydrochloric acid. A mixture of 10.0 g of silica (mesh size 0.2–0.3 μm) & 40 ml of 1 M hydrochloric acid was added in a 100 ml round-bottomed flask with a stirrer bar and stirring continued for 5 h at room temperature, the pretreated silica was collected by filtration, washed with distilled water until the pH was more than 6.0; then dry in an oven at 100 °C for 5 h. Then impregnation of phosphotungstic acid was done. Phosphotungustic acid 1.2 g, pretreated silica 2.0 g, and 20 ml of distilled water were put into a 100 ml flask, the resulting mixture was refluxed by stirring in an oil bath for 5 h at 100 °C, then evaporated to dryness at 90 °C, and further dry in an oven at 100 °C for 5 h.

2.3. Catalyst characterization methods

FT-IR spectra of catalyst were recorded by using a Varian 2000 IR spectrometer by employing the KBr pellet technique. X-ray diffraction patterns of pure silica and catalyst were obtained by using a powder XRD patterns were noted on a RigakuMiniflex (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å) with a 20 min^{-1} scan speed and a scan range of 5-80° at 30 kV and 15 mA. Energy Dispersive X-ray spectrometry (EDX) of prepared material gave information for elemental study which was determined using SEM instrument combined with an INCA instrument for energy dispersive X-ray spectroscopy-scanning electron microscopy (EDX-SEM), with scanning electron electrode at 20 kV.

2.4. General reaction procedure for synthesis of pyrazolopyranopyrimidines derivative by using Si-PTA catalyst

A mixture of Barbituric acid (1 mmol), aryl aldehyde (1 mmol), 3-methyl-1-phenyl-5-pyrazolone (1 mmol) & 10 wt% Si-PTA catalyst were added in 50 ml RBF containing 5 ml EtOH /H_2O and the mixture were heated under reflux for the appropriate time. The progress of the reaction was monitored with help of TLC. After completion of the reaction, the mixture was cooled and the precipitate was filtered, dried and dissolved it in hot ethanol in order to separate the catalyst from product. Finally, pure product was obtained by recrystallization from hot ethanol.

2.5. Spectral data of representative compounds (4-b to 4-h)

2.5.1. 3-methyl-4-(4-nitrophenyl)-1-phenyl-6,8-dihydropyrazolo [4′,3′:5,6]pyrano[2,3-d]pyrimidine-5,7-(1H,4H)-dione(**4-b**)

M.P: 230–232 °C; IR (KBr, in cm^{-1}): 3284, 3116, 1666,1597, 1566, 1460 and 1274; ^{1}H NMR (DMSO, in δ ppm): 10.16 (s,1H), 9.16 (s,1H), 8.07–8.12 (d,2H), 7.61–7.65(d,2H), 7.12–7.37(m, 5H), 4.85 (s,1H), 2.20 (s,3H); ^{13}C NMR (DMSO, in δ ppm): 162.00, 153.90, 150.70, 147.70, 142.90, 140.70, 137.16, 133.89, 131.40, 129.20, 128.82, 126.20, 120. 53, 118.21, 104.89, 81.10, 40.31, 30.28, 11.77; MS (*m*/*z*): 417 (M^+, 100 %),

2.5.2. 4-(4-Hydroxyphenyl)-3-methyl-1-phenyl-6,8-dihydropyrazolo [4′,3′:5,6]pyrano[2,3-d] pyrimidine-5,7-(1H,4H)-dione(**4-c**)

M.P: 254–256 °C; IR (KBr, in cm^{-1}): 3278, 3120, 2989, 1693, 1589, 1249; ^{1}H NMR (DMSO, in δ ppm): 11.21 (s, 1H), 9.13 (s, 1H), 7.65–7.75 (d, 2H), 7.50 (d, 2H), 7.35–7.45(t, 1H), 6.90 (d, 2H), 6.62–6.65 (d, 2H), 5.30 (s,1H), 4.75 (s,1H), 1.95 (s,3H), ^{13}C NMR (DMSO, in δ ppm): 163.02, 154.00, 151.71, 148.40, 137.41, 135.30, 130.40, 128.70, 122.36, 118.22, 112.18, 81.20, 32.20, 13.06, MS (*m*/*z*): 388 (M^+,100 %).

2.5.3. 4-(3,4-Dimethoxyphenyl)-3-methyl-1-phenyl-6,8-dihydropyrazolo[4′,3′:5,6] pyrano- [2,3-d] pyrimidine-5,7-(1H,4H)-dione(**4-e**)

M.P: 270–272 °C; IR (KBr, in cm^{-1}): 3213, 3080, 1678, 1595, 1274; ^{1}H NMR (DMSO, in δ ppm): 10.37 (s,1H), 8.85 (s,1H), 7.80 (d,2H), 7.64 (d,2H), 7.45 (t,1H), 6.95–7.02 (s,1H), 6.78 (d,1H), 6.63 (d,1H), 4.85 (s,1H), 3.89 (s,3H), 3.86 (s,3H), 2.32 (s,3H); ^{13}C NMR (DMSO, in δ ppm): 164.52, 162.80, 161.22, 155.90, 154.15, 150.72, 148.7, 148.32, 132.20, 125.84, 117.30, 115.70, 111.62, 56.30, 56.00, 55.92, 10.53; MS (*m*/*z*): 432 (M^+,100 %).

2.5.4. 4-(2,4-Dichlorophenyl)-3-methyl-1-phenyl-6,8-dihydropyrazolo[4′,3′:5,6]pyrano[2,3-d] pyrimidine-5,7-(1H,4H)-dione(**4-g**)

M.P: 234–235 °C; IR (KBr, in cm^{-1}): 3223, 3143, 3076,1739, 1695, 1541, 1390, 804; ^{1}H NMR (DMSO, in δ ppm): 9.76–10.0 (s,1H), 8.91 (s,1H), 7.89–7.92 (d,2H), 7.67–7.70 (d,2H), 7.55 (t,1H), 7.12–7.29 (m,3H), 5.03(s,1H), 2.16 (s,3H); ^{13}C NMR (DMSO, in δ ppm): 162.10, 155.92, 150.23, 147.72, 142.90, 139.10, 137.16, 135.32, 132.80, 130.89, 129.60, 127.82, 126.20, 122.53, 118.21, 82.04, 32.15, 12.22; MS (*m*/*z*): 440 (M^+,100 %).

*2.5.5. 4-(4-Chlorophenyl)-3-methyl-1-phenyl-6,8dihydropyrazolo [4′,3′:5,6]pyrano[2,3-d]pyrimidine-5,7-(1H,4H)-dione(**4-h**)*

M.P: 225 °C; IR (KBr, in cm^{-1}): 3215, 3054, 1686, 1623, 1588, 1488, 1369, 836, 870; ^1H NMR (DMSO, in δ ppm): 10.19 (s, 2H), 7.27 (d, 2H), 7.06 (d, 2H), 7.35–7.45(t,1H), 7.50 (d,2H), 7.65–7.75 (d,2H), 5.41(s, 1H), 2.23 (s, 3H); ^{13}C NMR (DMSO, in δ ppm):160.35, 150.57, 141.58, 134.64, 129.92, 128.59, 128.06, 127.71, 127.27,89.45, 30.16, 9.96; MS (*m*/*z*):406 (M^+, 100 %),

3. Results and discussion

3.1. Catalyst characterization

3.1.1. FT-IR analysis of prepared materials

The characteristic bands for keggin structure of HPW (phosphotungstic acid) are exhibited at 1080, 985, 890 and 839 cm^{-1}. All the characteristic bands of keggin structure are observed at the same wave number in prepared catalyst which indicates the preservation of the basic kegging structure in the silica-supported phosphotungstic acid catalyst. Fig. 1, shows the band at 1080 and 890 $cm^{-1}$are more intense in Si-PTA compared to pure silica; it confirms the presence of the undegraded anion of the catalyst. A strong peak at close to 3400 indicates the presence of silica impregnated with phosphotungstic acid (see).

3.2. XRD analysis of catalysts

The XRD pattern of pure silica and silica-supported phosphotungstic acid is shown in Fig. 2. Silica displays a broad band centered at 2θ = ∼25°. When phosphotungstic acid was impregnated with silica, the characteristic peaks assigned to PTA are comparable to those for the Si-PTA, which implies retention of their crystalline character. As seen in Fig. 2, reduction in the peak of Si-PTA was exhibited at 25° compared to silica which indicates the surface of silica was accumulated by particles of phosphotungstic acid in the impregnation method. Obtained intense peaks indicate that there is no significant change in the structure of phosphotungstic acid and silica structures during preparation of catalyst, confirmed by XRD.

3.3. FE-SEM and Elemental analysis (EDX) of Si-PTA

The surface structures of Si-PTA catalyst were studied using SEM analysis. In the morphology study of pure Si, no agglomeration of particles occurred, while Si-PTA showed the agglomeration

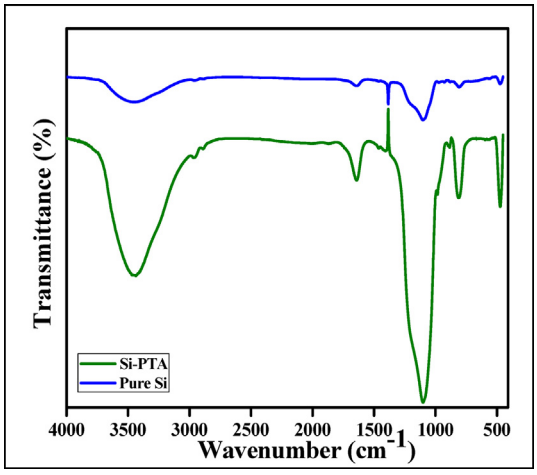


Fig. 1. FT-IR analysis of pure Si and prepared Si-PTA catalyst.

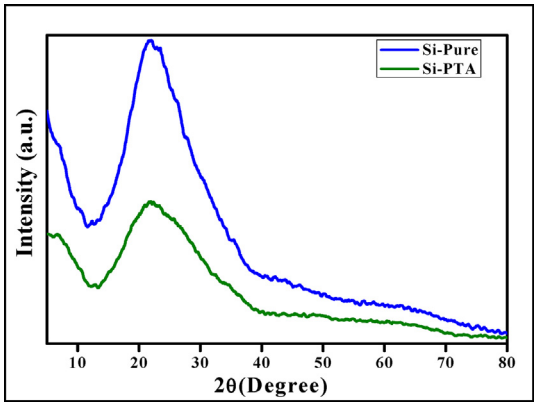


Fig. 2. XRD analysis of pure Si and prepared Si-PTA catalyst.

of particles, it reveals that uniform distribution of phosphotungstic acid on silica in prepared material and slight agglomeration occurred. Moreover, the Elemental analysis was studied by energy dispersive X-ray spectroscopy. EDS mapping of pure silica showed the presence and uniform distribution of silicon and oxygen throughout the structure. Further, the presence of Si, W, P and O elements in the catalyst was observed by EDX mapping and a uniform distribution was also observed (the second image of Fig. 3).

3.4. Catalyst activity

To find out suitable reaction conditions for the synthesis of the Pyrazolopyranopyrimidines, several experiments were conducted and develop multicomponent condensation reaction of Barbituric acid, 3-methyl-5-pyrazolone and Benzaldehyde in presence of Si-PTA. In order to find the optimum conditions for this reaction, initially, the effect of solvent, temperature, amount of catalyst, and reaction time was tested. As per the results summarized in Table 1, the catalyst effect on reaction rate and yield was investigated, and find out the reaction cannot proceed without a catalyst in presence of different solvents at room temperature for up to several hours (Table 1, entries from 1 to 6). As shown in Table 1, good to efficient yield was obtained when the reaction was conducted at reflux temperature in ethanol: water (1:1) solvent system (Table 1, entry 7) in a short reaction time. However, the same reaction continues for a longer time in ethanol: water (1:1) under reflux temperature obtains a low yield (Table 1, entries 8–10). One more experiment was carried out in presence of the catalyst under solvent-free conditions the reaction proceeded with a lower yield of product (Table 1, entry 13). Obtained results in Table 1 shows that the reaction proceeded highly efficiently with a high yield in a polar solvent and become sluggish and low yield in nonpolar solvent. In the final, we conclude that reflux temperature in ethanol: water (1:1) solvent system with 10 wt% of catalyst is highly effective for this reaction and same has been considered for further study.

Si-PTA is a selective heterogeneous catalyst in the synthesis of Pyrazolopyranopyrimidines in ethanol: water under reflux conditions. The next examination was a screening of the effect of catalytic amount on the conversion of reactants. The results of catalytic screening as shown in Table 1 (Entry7-9), it was showed 10 wt% of catalyst is sufficient for complete conversion with maximum yield (Entry 7). With the decrease in the amount of catalyst up to 5 wt%, the yield was also decreased and more time was required for the completion of the reaction (Entry 9). However, an increase in the amount of catalyst up to 20 wt% does not affect the yield as well rate of reaction (Table 1, Entry 8) and hence 10 wt % of Si-PTA was selected for further investigation to compare the

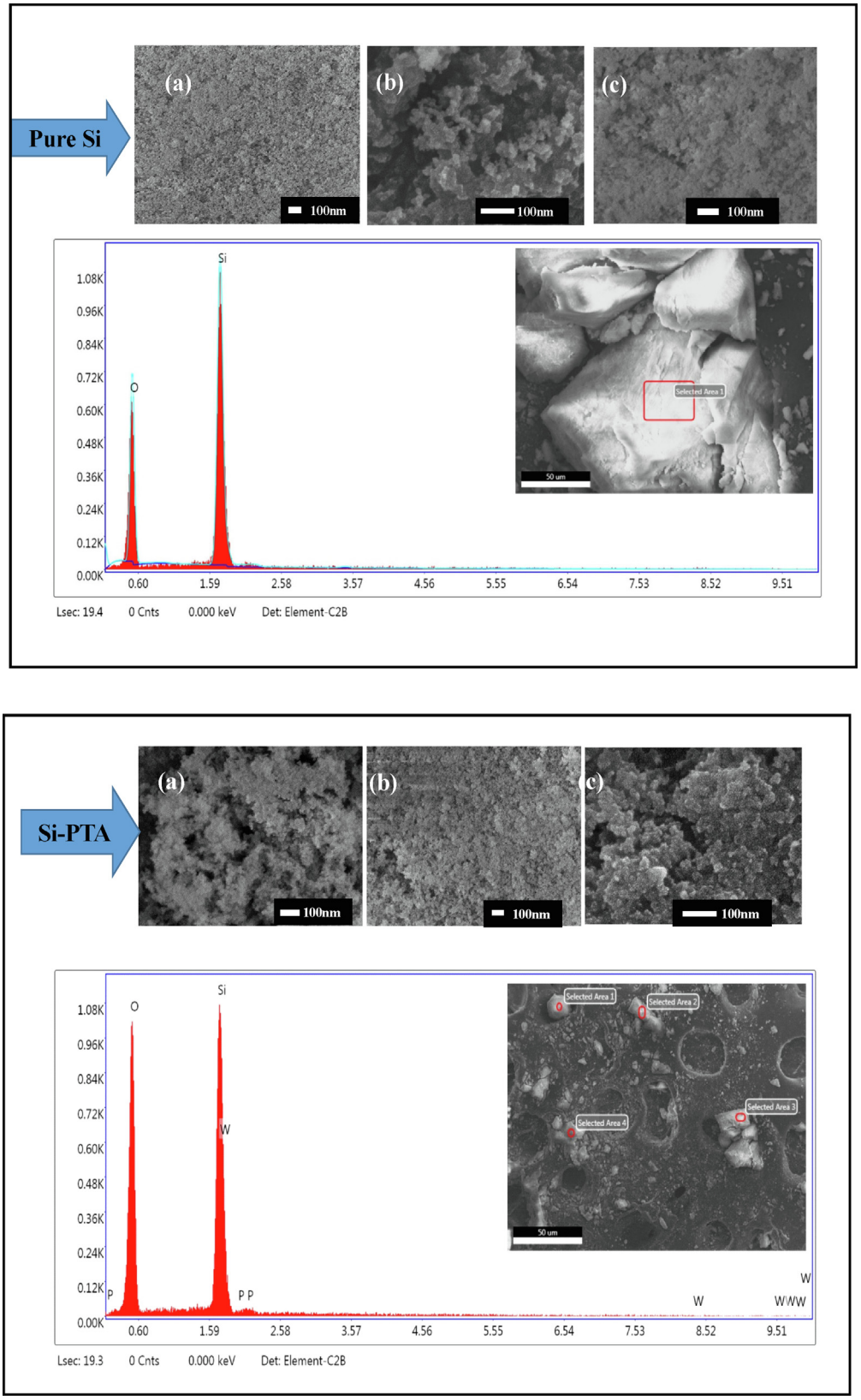
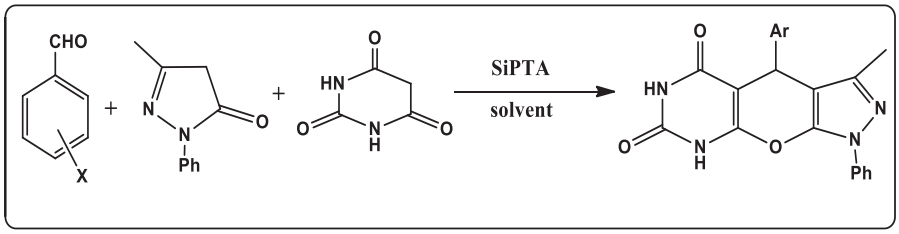


Fig. 3. FE-SEM and Elemental analysis (EDX) of pure Si and Si-PTA.

Table 1
Optimization of reaction conditions for the synthesis of Pyrazolopyranopyrimidines[a].



Entry	Solvent	Cat.(wt%)	Temp.(°C)	Time(hr)	Yield (%)[b]
1	Toulene	10	Reflux	04	50
2	DCM	10	Reflux	04	58
3	CH_3CN	10	Reflux	04	65
4	MeOH	10	Reflux	01	75
5	EtOH	10	Reflux	01	80
6	H_2O	10	Reflux	01	78
7	EtOH: H_2O	10	Reflux	01	96
8	EtOH: H_2O	20	Reflux	01	96
9	EtOH: H_2O	05	Reflux	02	80
10	EtOH: H_2O	–	Reflux	04	50
11	EtOH: H_2O	10	RT	04	60
12	EtOH: H_2O	10	60 °C	24	82
13	—	10	RT	24	45

Reaction conditions:(a) Barbituric acid (1 mmol), aryl aldehyde (1 mmol), 3-methyl-1-phenyl-5-pyrazolone (1 mmol); In presence of Catalyst; Reaction completion was monitored by TLC.(b) Isolated yield.

effectiveness of various catalysts in the synthesis of pyrazolopyranopyrimidines.

As evidently shown in Table 2, the yield obtained using different reported catalyst were found comparatively low. The comparison of the catalytic activity of Si-PTA and oleic acid clearly shows, SI-PTA can catalyze the reaction with a higher yield of desired product within a short reaction time. OMWCNTs, DABCO, & [BNPs-Caff] HSO_4catalysts exhibit high and comparable catalytic activities but slightly lower than that of Si-PTA (Table 2, entry 1, 2, 3, 5 respectively) with lots of weaknesses in the reaction.

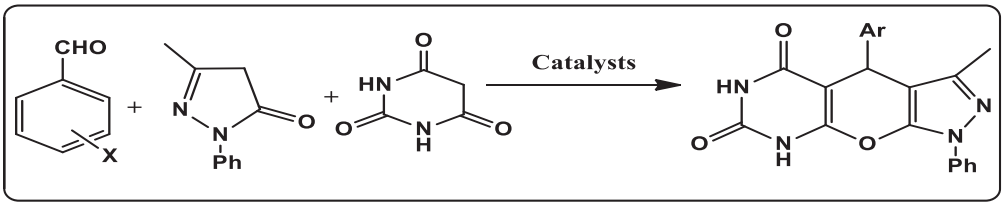
With results in hand, we were encouraged to examine the scope and generality of this method using a variety of substituted aryl aldehydes. Thus various aromatic and heteroaromatic aldehydes were reacted with 3-methyl-5-pyrazolone and barbituric acid; the obtained experimental results are tabulated in Table 3 (entries 1–10). As seen in Table 3, it is evident that, most of the reactions were performed with a good to high yield of pyrazolopyranopyrimidines. Aromatic aldehydes bearing electron withdrawing and electron donating group reacts under optimized conditions, and the corresponding products are obtained in good to high yield. In general comparison, aromatic aldehyde containing electron withdrawing group as well as heteroaromatic aldehydes reacts to produce a high yield (Table 3, entry 2, 10, 11), while aromatic aldehydes containing electron donating group react to provide a comparatively low yield (Table 3, entry 3, 6).

3.5. Proposed reaction mechanism

3.5.1. Plausible SiPTA catalyzed reaction mechanism for synthesis of pyrazolopyranopyrimidines

We believe that, at first, the catalyst interacts with the oxygen atom of the carbonyl group of Barbituric acid and forced it to convert into enol form. In the next step, the catalyst protonates oxygen of the carbonyl group of aromatic aldehyde and makes carbon electrophilic which fascinates nucleophilic attack results in C—C bond formation followed by dehydration. Further, 3-methyl-5-pyrazolone (IV-f) undergoes tautomerization to form compound (IV-e), it is the most prominent candidate for cyclization. Finally

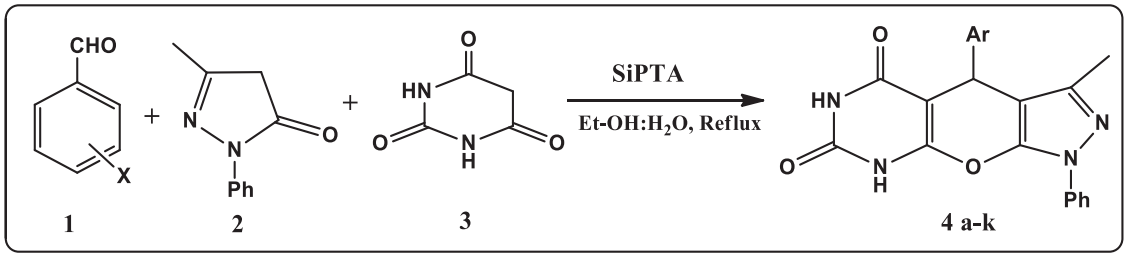
Table 2
Comparisons of various catalysts with Si-PTA in the synthesis of Pyrazolopyranopyrimidines[a].



Entry	Catalyst	Time(min)[e]	Yield (%)[f]
1	OMWCNT's	70	94
2	DABCO	45	84
3	[BNPsCaff]HSO_4	50	85
4	Oleic acid	120	78
5	Si-PTA	60	96 [present work]

Reaction conditions: (a) Synthesis of pyrazolopyranopyrimidine from Barbituric acid, 3-methyl-5- pyrazolone and aryl aldehydes under optimized reaction condition, (b) catalyst amount 10 wt%.
(c) Solvent: EtOH:H_2O (1:1). (d) Reflux temperature, (e) reaction time is monitored by TLC.(f) Isolated yield.

Table 3
Synthesis substituted Pyrazolopyranopyrimidines derivatives using Si-PTA under optimized reaction conditions.



Entry	Aldehyde	Product code	Time (hr)	Yield (%)[b]
1.	Benzaldehyde	4-a	01	96
2.	p-nitrobenzaldehyde	4-b	01	96
3.	4-hydroxybenzaldehyde	4-c	01	90
4.	4-hydroxy-3-methoxy benzaldehyde	4-d	01	92
5.	3,4-Dimethoxy benzaldehyde	4-e	01	94
6.	4-Methyl benzaldehyde	4-f	01	88
7.	2,4-Dichlorobenzaldehyde	4-g	01	91
8.	4-Chlorobenzaldehyde	4-h	01	89
9.	2-Hydroxybenzaldehyde	4-i	01	90
10.	3-Bromobenzaldehyde	4-j	01	94
11.	4-Flurobenzaldehyde	4-k	01	92

(a) All reactions were conducted using 1 mmol reactant (1,2&3) and 10 wt% catalyst in EtOH:H_2O(1:1) at reflux temperature. (b) Isolated yield.

nucleophilic addition of compound (IV-e) on compound (IV-d) followed by cyclization and then dehydration to gave 3-methyl-4-(phenyl)-1-phenyl-6,8-dihydropyrazolo [3-6]pyrano[2,3-*d*] pyrimidine-5,7(1*H*,4*H*)-dione. In this reaction, Si-PTA plays an important role in cyclization as well as dehydration due to which we achieved our target with efficiency, after completion of the reaction catalyst can be removed easily and utilized in many more reactions. However, further catalyst characterization and in-depth correlation for the catalyzed mechanism are under study.

3.6. Recyclability test of Si-PTA

The advanced, highly efficient, and recyclable heterogeneous catalyst for the synthesis of pyrazolopyranopyrimidines derivatives is the ultimate objective of our research. It is essential to know the stability of heterogeneous catalysts at given reaction conditions. In order to know the reusability of the catalyst, we separated the Si-PTA catalyst from reaction mixture by simple filtration and washed it two to three times using water and ethanol to remove all types of impurities and reused it for further successive five cycles. Recyclability test reveals that, no significant loss in the yield of pyrazolopyranopyrimidines. Moreover, complete conversion of the reactant with a comparable yield of product was maintained during the recycling test of Si-PTA. Further study and comparison of fresh and recycled catalysts is going on and some other applications are in process.

4. Conclusions

We have prepared a heterogeneous Si-PTA catalyst and characterized it completely by different spectroscopic and analytical techniques. After the successful characterization of the catalyst, it was utilized in the synthesis of pyrazolopyranopyrimidines derivatives from barbituric acid, 3-methyl-5-pyrazolone and substituted aryl aldehydes under optimized reaction conditions. The catalyst showed 96–88 % isolated yield of product with maximum purity. Finally, the catalyst was recycled by simple filtration and reused up to five cycles without loss of catalytic efficiency during the experimental procedure. Silica-supported phosphotungstic acid exhibits key advantages such as simplicity, recyclability, and efficiency.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] Y. Ogiwara, K. Takahashi, T. Kitazawa, N. Sakai, Indium (III)-catalyzed knoevenagel condensation of aldehydes and activated methylenes using acetic anhydride as a promoter, J. Org. Chem. 80 (6) (2015) 3101–3110.
[2] G. Jones, The knoevenagel condensation, Org. React. 15 (1967) 204–599.
[3] N. Mase, T. Horibe, Organocatalytic knovengel condensation by means of carbamic acid ammonium salt, Org. Lett. 15 (2013) 1854–1857.
[4] H. Shaterian, M. Arman, F. Rigi, Domino knovengel condensation, michael addition, and cyclization using ionic liquid,2-hydroxyethyl ammonium formate as recoverable catalyst, J. Mol. Liq. 158 (2011) 145–150.
[5] O.H. Qareaghaj, S. Mashkouri, M.R. Naimi-Jamal, G. Kaupp, Ball milling for quantitative and for specific knovengel condensation+Michael addition cascade in the synthesis of various-2amino-4-aryl-3-cyano-4H-Chromenes without heating, RSC Adv. 4 (2014) 48191–48201.
[6] J. Quiroga, C. Cisneros, B. Insuasty, R. Abonia, M. Nogueras, A. Sánchez, A regiospecific three-component one-step cyclocondensation to 6-cyano-5,8-dihydropyrido[2,3- d]pyrimidin-4(3H)-ones using microwaves under solvent-free conditions, TetrahedronLett. 42 (33) (2001) 5625–5627.
[7] P.J. Chen, A. Yang, Y.F. Gu, X.S. Zhang, K.P. Shao, D.Q. Xue, P. He, T.F. Jiang, Q.R. Zhang, H.M. Liu, Synthesis of in vitro antimicrobial and cytotoxic activities of novel pyrimidine benzimidazole combination, Bioorg. Med. Chem. Lett. 24 (2014) 2741–2743.

[8] A.M. El-Agrody Fouda, A.A. Al-Dies, Studies on synthesis, in vitro antitumor activity of 4-H-benzochromenes, 7H-benzochromene [2,3-d] pyrimidines derivative and structure activity relationship of 2,3-positions and fused rings at 2,3-positions, Med. Chem. Res. 23 (2014) 3187–3199.
[9] S. Mert, R. Kasimogullari, T. Ica, F. Colak, A. Altun, S. Ok, Synthesis structure activity relationship, and in vitro antibacterial and antifungal activity evaluation of pyrazole carboxylic acid and dicarboxylic acid derivatives, Eur. J. Med. Chem. 78 (2014) 86–96.
[10] J.V. Faria, P.F. Vegi, A.G.C. Miguita, M.S. dos Santos, N. Boechat, A.M.R. Bernardino, Recently reported biological activities of pyrazole compounds, Bioorg. Med. Chem. 25 (21) (2017) 5891–5903.
[11] H.S. Chung, Y. Kim, S.J. Oh, H. Kim, S.I. Choi, Y. Zhang, J.H. Jeong, H. Bae, A synthetic compound 4-acetyl-3-methyl-6-(3,4,5-trimethoxyphenyl) pyrano [3,4-c]pyran-1,8-dione, ameliorates ovalbumin-induced asthama, Bioorg. Med. Chem. 21 (2013) 6359–6365.
[12] S. Karpov, Y. Kayukov, A. Grigorev, V. Tafeenko, et al., Synthesis and solid state luminescence of highly substituted 6-amino-2-H pyran-2-one derivative, Tetrahedron. Lett. 61 (2020).
[13] Y.R. Prasad, A.L. Rao, L. Prasoona, K. Murali, P.R. Kumar, Synthesis and antidepressant activity of some 1,2,3-triphenyl -2-pyrazoline and3-(2"-hydroxynapthalene-1"-yl)-1,5-diphenyl-2-pyrazoline, Bioorg. Med. Chem. Lett. 15 (2005) 5030–5034.
[14] Z.H. Ismail, G.M. Aly, M.S. El-Degwi, H.I. Herba, M.M. Ghorab, Synthesis and insecticidal activity of some pyranopyrazole, pyrazolopyranopyrimidines and pyrazolopyranopyridines, J. Egypt Bio. 13 (2003) 73–82.
[15] V.K. Ahluwalia, A. Dahiya, V. Garg, Reaction of 5-amino-4-formyl-3-methyl (or phenyl)-l- phenyl-lH- pyrazoles with active methylene compounds: Synthesis of fused heterocyclic rings, Indian J. Chem. 36B (1997) 88–90.
[16] J.L. Wang, D. Liu, Z.J. Zheng, S. Shan, X. Han, S.M. Srinivasula, C.M. Croce, E.S. Alnemri, Z. Huang, Structure based discovery of an organic compound that bind Bc 1–2 protein and induces apoptosis of tumor cells, Proc. Natl. Acad. Sci. U.S.A. 97 (2009) 7124–7129.
[17] E.M. Grivsky, S. Lee, C.W. Sigel, D.S. Duch, C.A. Nicol, Synthesis and antitumor activity of 2,4-diamino-6-(25-dimethoxybenzyl)-5-methylpyrido[2,3-d] pyridine, J. Med. Chem. 23 (1980) 327–329.
[18] N.R. Kamdar, D.D. Haweliwala, P.T. Mistry, S.K. Patel, Design synthesis and invitro evslustion of antitubercular and antimicrobial activity of some novel pyranopyrimidines, Eur. J. Med. Chem. 45 (2010) 5056–5063.
[19] H.M. Aly, M.M. Kamal, Efficient one pot preparation of novel fused chromeno [2,3-d] pyrimidine and pyrano [2,3-d] pyrimidine derivatives, Eur. J. Med. Chem. 47 (2012) 18–23.
[20] Y. Ren, B. Liu, Z. Zhang, J. Lin, Silver exchanged heteropolyacid catalyst: An efficient heterogeneous catalyst for synthesis of 5-ethoxymethylfurfural from 5-hydroxymethylfurfural and fructose, J. Ind. Eng. Chem. 21 (2015) 1127–1131.
[21] B. Yang, J.J. Pignatello, D. Qu, B. Xing, Reoxidation of photoreduced polyoxotungustate by different oxidant in presence of a model pollutant. Kinetica and reaction mechanism, J. Phys. Chem. A 119 (2015) 1055–1065.
[22] S. Sadjadi, M.M. Heravi, Recent advances in applications POMs and their hybribds in catalysis, Curr. Org. Chem. 20 (2016) 1404–1444.
[23] S.H. Teo, M. Goto, Y.H. Taufiq-Yap, Biodiesel production from Jatropa curcas L. oil with Ca and La mixed oxide catalyst in near supercritical methanol conditions, J. Supercrit. Fluids 104 (2015) 243–250.
[24] A. Escobar, A. Sathicq, L. Pizzio, M. Blanco, G. Romanelli, Biomass valorization derivatives: Clean esterification of 2-furoic acid using tungustophospheric acid/zirconica composite as recyclable catalyst, Process Saf. Environ. Prot. 98 (2015) 176–186.
[25] H. Eshghi, A. Javid, A. Khojastehnezhad, F. Moeinpour, F.F. Bamoharram, M. Bakavoli, M. Mirzaei, Preyssler heteropolyacid supported on silica coated NiFe2O4 nanoparticle for the catalytic synthesis of bis (dihydropyrimidinones) benzene and 3,4-dihydropyrimidine-2-1H-ones, Chin. J. Catal. 36 (2015) 299–307.
[26] M.S. Tiwari, G.D. Yadav, Kinetics of Friedel craft benzoylation of veratrole benzoic anhydride using $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 solid acid catalyst, Chem. Eng. J. 266 (2015) 64–73.
[27] L. Hong, Y. Gui, J. Lu, J. Hu, J. Yuan, L. Niu, High performance of polyoxometalate/ Pt, Pd nanoparticle/carbon nanotube electrocatalyst for methanol electrooxidation, Int. J. Hydrogen Energy 38 (2013) 11074–11079.
[28] Y. Zhu, M. Zhu, L. Kang, F. Yu, B. Dai, Phosphotungustic acid supported on mesoporous graphitic carbon nitride as catalyst for oxidative desulfurization of fuel, Ind. Eng. Chem. Res. 54 (2015) 2040–2047.
[29] V. Kozhevnikov, Friedel craft acylation and related reaction catalyzed by heteropolyacid, Appl. Catal. A: General. 256 (2003) 3–18.
[30] S. Cao, W. Zeng, S. Wang, T. Zhang, Z. Liu, X. Xie, Silica supported phosphotungustic acid as green heterogeneous catalyst for α-pinene polymerization, Adv. Res. Materials 781–784 (2013) 448–451.
[31] Z. Liu, S. Cao, S. Wang, W. Zeng, T. Zhang, Silica supported phosphotungustic acid as novel heterogeneous catalyst for β-pinene polymerization, Reac. Kinet. Mech. Cat. 111 (2014) 577–590.
[32] X.-T. Li, A.-D. Zhao, L.-P. Mo, Z.-H. Zhang, Z.-H. Zhang, Meglumine catalyzed expeditious four component domino protocol for synthesis of pyrazolopyranopyrimidines in aqueous medium, RSC Adv. 4 (93) (2014) 51580–51588.
[33] G.M. Ziarani, F. Aleali, N. Lashgiri, A. Badiei, A. Abolhasani, Efficient synthesis and antimicrobial evaluation of prazolopyranopyrimidines in the presence of SBA-Pr-SO_3H as a nanoporus acid catalyst, Iran. J. Pharm. Res. 17 (2018) 525–534.
[34] M. Pirhayati, A. Kakanejadifard, H. Veisi, A new nano Fe3O4-supported organocatalyst based on 3, 4-dihydropyridine: an efficient heterogeneous nanocatalyst for one pot synthesis of pyrazolopyridines and pyranopyrimidines, Appl. Organometal. Chem. 30 (2016) 1004–1008.