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NANO-FERRITE SUPPORTED GLUTATHIONE AS A REUSABLE NANO-ORGANOCATALYST FOR THE SYNTHESIS OF PHTHALAZINE-TRIONE AND DIONE DERIVATIVES UNDER SOLVENT FREE CONDITION

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Abstract:

Nano-organocatalyzed one-pot four component reaction for the synthesis of phthalazine-triones/diones derivatives have been devised for the first time from easily accessible starting materials under solvent free conditions. This methodology showed very good substrate scope and high degree of tolerance for a variety of aldehydes (including aliphatic and hetero-arometic aldehydes) and active methylene compounds. More over the catalyst can be easily separated from the reaction mixture because of its highly paramagnetic nature, by using an external magnet and can be reused in five more consecutive runs without much decrease in catalytic activities. Other significant advantages of this method are shorter reaction time, good yield, simple work-up procedure and easy catalyst handling etc.

Keywords: Nano-organocatalyst, solvent free reaction condition, one-pot MCR, reusability of catalyst.

Introduction

Organocatalysis, the term which refers to a form of catalysis where the rate of the reaction is increased by the addition of an organic catalyst is an attractive and productive enterprise in the modern day chemistry. Fabrication, characterization, modification and application of organocatalyst is an emerging field which is extensively applied on many name reactions like Michael reaction,[1] Mannich reaction,[2] enantioselective C-N, C-C, C-O bond formation etc,[3] but their separation and reusability are the major drawbacks. So, there is a lack of its application under sustainable circumstances. Nanoparticles are striking candidates as solid supports for immobilization of homogeneous organocatalyst like glutathione,[4] L-proline,[5] dopamine,[6] sulphonic acids etc.[7,8] Out of other solid supports like silica, allumina, metal oxides, polymers etc

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nanoparticles are non-arguably most widely investigated because its separation and reusability are easy. Green chemistry has fascinated substantial attention for overcoming several troubles relating to environmental pollution. Application of heterogeneous nano-organocatalyst is considered as a sustainable approach because: (i) nano-organocatalysts are well dispersed in reaction medium thereby providing high surface area for readily access of substrate molecules and (ii) these can be easily separated from the reaction mixture by filtration, centrifugation or by using an external magnetic field, which is then reused in several more consecutive runs without much decrease in catalytic activity. Metal nanoparticles attached to enzymes or bio-molecules are newer class of catalysts with excellent activities in diversity orientated synthesis (DOS) of small molecules having skeletons found in many important natural products.[9,10]

Heterocyclic compounds possessing aza group are widely distributed in nature and out of a large number of N-containing compounds, those which possess hydrazine moiety at the fusion site are of immense importance because of their pharmacological, clinical and agrochemical applications.[11,12] Many of these phthalazine derivatives possess anti-fungal,[13] anti-cancer,[14] anti-tumor[15] and many other pharmaceutical activities.[16] Because of these biological and medicinal activities many researchers developed powerful and promising method for synthesizing phthalazene molecules by using various types of catalysts like inorganic–organic hybrid materials Al-SBA-15-TPI/$H_6P_2W_{18}O_{62}$,[17] TBBDA,[18] Cs_2CO_3@magnetic nanoparticles,[19] SO_3H-FMSM,[20] SBA@$BiPy^{2+}2Cl^-$,[21] [TMG][Ac],[22] RH@[SiPrDABCO@$BuSO_3H$]HSO_4,[23] $CoFe_2O_4$-CS-SO_3H[24] etc in by sequential multi-component reaction (MCR). These reported methods possess many advantages but at the same time encounters many disadvantages too. Previously our group also reported Ni (0) NPs catalyzed synthesis of phthalazine derivatives[25] but major difficulties were agglomerisation of Ni-NPs and unable to form phthalazine molecules with aliphatic and heteroaromatic aldehydes. To adress these problems, we applied surface stabilized magnetic nano-organocatalyst. By this way we prevented the chance of agglomerisation and increased the catalytic activity of nano-composite. From literature study we have chosen glutathione as a stabilizer as well as organocatalyst, because it binds to nanoparticles by using –SH functionality while $–NH_2$ and –COOH groups are free for catalysis.[10] Furthermore, for easy separation we have selected magnetic nanoparticles (Fe_3O_4) which avoids the involvement of cumbersome procedure like centrifugation and filtration. Moreover application of nano-FGT also made the methodology more efficient as compared to the one reported, since the reaction went

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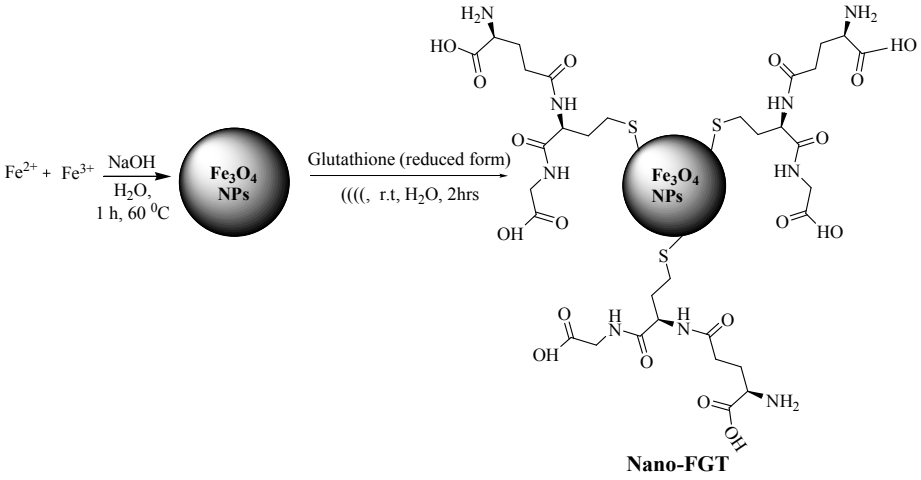
smoothly with a diverse range of active methylene compounds and aldehydes including heteroaromatic and aliphatic aldehydes.

So, the chief purpose behind this presented protocol is to highlight the synergetic effects of combined nano-organocatalyst operated synthetic enhancement procedure, MCR and solvent free reaction condition for development of new eco-compatible methodology. Therefore, we have chosen nano-FGT (nano-ferrite on glutathione) as a proficient, harmless, mild, magnetically recyclable, highly stable, powerful solid nano-organocatalyst and have applied that for the synthesis of phthalazine derivatives by four components MCR under solvent free conditions.

Results and discussion:

Magnetic nano-FGT, consist of Fe_3O_4 spheres as the core and glutathione as the outer shell and it was prepared by a simple, low cost and convenient methods.[4] Magnetite nanoparticles were synthesized by the co-precipitation of Fe^{2+} and Fe^{3+} in ammonia solution.[26] To improve the chemical stability of magnetite nanoparticles, their surface modification was successfully performed by the suitable deposition of glutathione onto nanoparticles surface by ultrasonic irradiation at room temperature (Scheme-1).



Scheme: 1 Synthesis of nano-FGT

Formation of nano-FGT was confirmed by FT-IR, TEM, SEM and EDX analysis. Its thermal stability was analyzed by TGA. Functional group identification was done by FT-IR technique. FT-IR spectrum of nano-FGT (Fig. SI 1) showed broad peaks at 3349 and 3166 cm^{-1} which indicated the presence of –OH and $–NH_2$ groups. The peaks at 1643 and 1634 cm^{-1} corresponds

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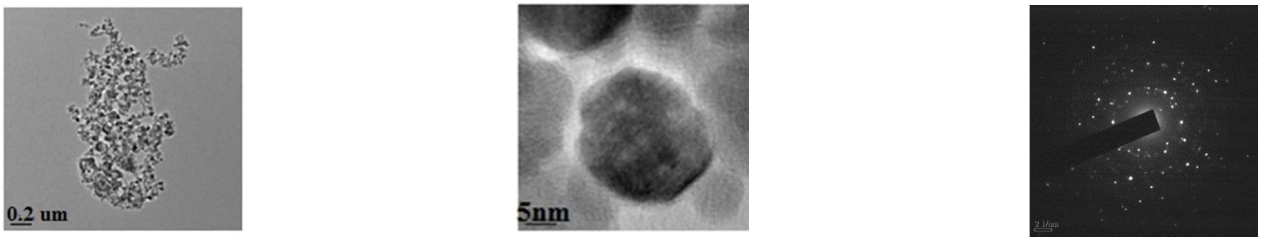
to the carbonyl stretching of acid and amide groups of glutathione respectively. Peak at 2926 cm^{-1} is due to C-H stretching. The absorption band at 599 cm^{-1} corresponds to Fe-O stretching of Fe_3O_4 NPs and absence of S-H stretching band at around 2525cm^{-1} clearly indicated that glutathione is successfully anchored on to the surface of Fe_3O_4 NPs via thiol group.[27] Morphology and particle size of nano-FGT was determined from TEM images. TEM images showed the presence of dark spherical nanoparticle core of size 10-20 nm uniformly coated with layer of glutathione [Fig. 1(a),(b)]. SAED (Selected Area Electron Diffraction) of freshly prepared nano-FGT showed spotty diffraction thereby proving its crystalline character [Fig 1 (c)]. EDX analysis was carried out to determine the elemental composition of nano-FGT. This confirmed the presence of Fe, O, S, N and C (Fig. 2). SEM images were obtained with the help of JSM-6360 (JEOL) scanning electron microscope. SEM image also confirmed the spherical morphology of nano-FGT (Fig. 3).



(a) (b) (c)

Fig. 1: (a) TEM images of nano-FGT at 0.2 µm, (b) at 5 nm (c) SAED pattern of nano-FGT

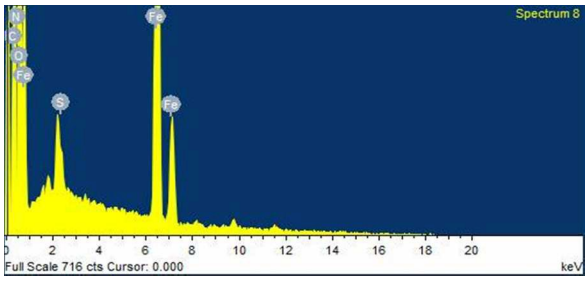


Fig. 2 : EDX of nano-FGT

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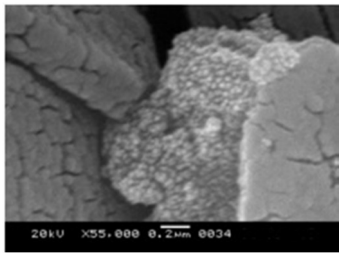

Fig. 3: SEM of nano-FGT at 200 nm

Prepared nano-FGT was also characterized by powder XRD technique. The XRD diffraction patterns shows characteristic 2Θ peaks at around 30.33, 35.61, 43.19, 57.28, 62.83, 74.30 which are in good agreement with that reported in literature.[4]

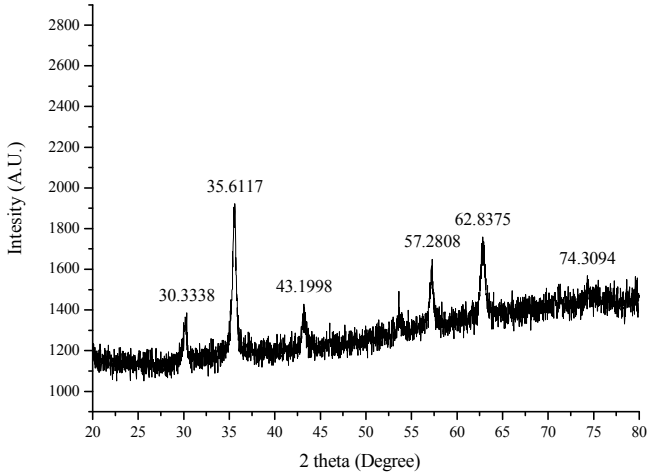

Fig. 4: Powder XRD pattern of nano-FGT

In order to gain information regarding thermal stability of nano-FGT, we performed TGA (Thermo Gravimetric Analysis). There is degradation at around 53 ^{0}C in the thermogram which corresponds to the degradation of solvent molecules trapped in the catalyst. There is another weight loss at 185 ^{0}C which is due to the degradation of glutathione molecule of nano-FGT. These observations proved that the catalyst is stable below 180 ^{0}C and therefore can be easily applied in reactions under that temperature (Fig. 5).

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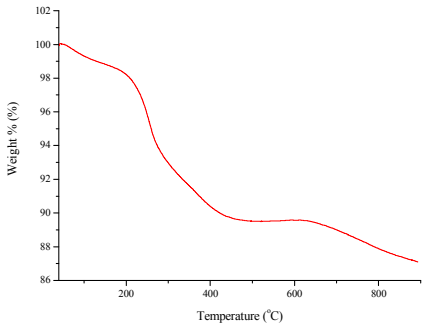

Fig. 5: Nano-FGT TGA thermogram.

ICP-OES analysis was performed in order to know the actual amount of Fe catalyst used in the nano-ferrite heterogeneous catalyst and it was found to be 63.23%.

After successful surface modification and characterization of nano-FGT, we explored its applicability for the synthesis of phthalazine dione and trione derivatives by four component condensation reaction of phthalic anhydride (**1**), hydrazinium hydroxide (**2**), active methylene compounds (**3, 4 or 5**) and aldehydes (**6a-q**) (**Scheme 2**). Initially a mixture of phthalic anhydride (**1**) (1 mmol), hydrazinium hydroxide (**2**) (1.2 mmol), dimedone (**3**) (1 mmol) and 4-chlorobenzaldehyde (**6a**) (1 mmol) was taken as a pilot reaction. Following which the reaction was allowed to stir at room temperature without any catalyst. It was found that without catalyst the reaction failed to form the desired product even after 24 h of constant stirring. Only starting materials were evidenced in the TLC. Then another new set of the reaction was set up with addition of nano-FGT which was stirred according to known procedures, [28] it is important to mention here that since the reaction is solvent free so, reactants and magnetic nano-organocatalyst (nano-FGT) were mixed properly by using a glass rod in to which a magnetic bit was added in order to maintain proper mixing during reaction period, which in turn increases the contact between the surface of the catalyst and reactant molecules. Firstly, the reaction was carried at room temperature, and to our delight it was found that after 12 h of continuous stirring desired product was forming but the conversion were very poor, most of the starting materials remained unreacted. This observation prompted us to apply thermal energy to the reaction. A number of reactions were set up in a pre-heated oil bath on a temperature controlled magnetic stirrer at different temperature ranging from 40-120 ^{0}C and the best result was obtained at 80 ^{0}C. However, no desired product was forming without addition of catalyst even at 80 ^{0}C after 24 h of stirring. All these observations proved the efficient role of catalyst in carrying out the reaction. The structure of the compound was identified by elemental and spectral analysis. IR spectrum of compound **15a** showed absorption bands at 1453 and 1109 cm^{-1} which are due to C-N and N-N

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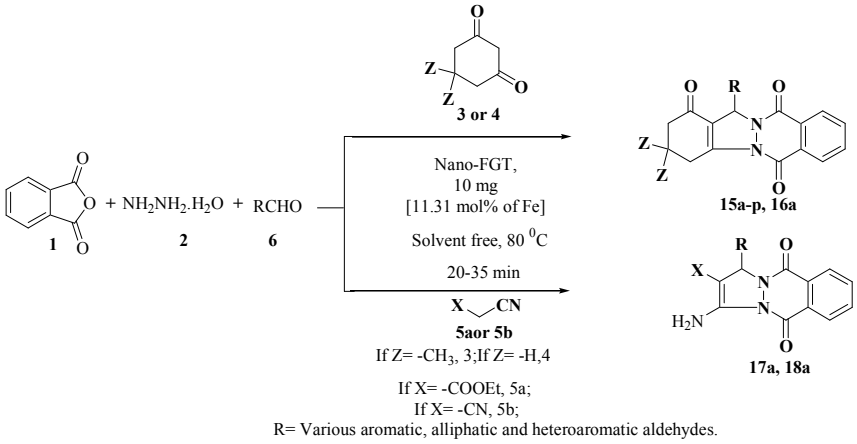
band stretching, band at 1666 cm^{-1} corresponds to carbonyl group of dimedone. In ^1H NMR of compound **15a** showed eight aromatic protons appear at δ 8.29-7.24. The methine proton was observed as a singlet at δ 6.34. The four methylene protons of the dimedone residue appeared as a AB system in δ 3.35-3.13 and singlet at δ 2.26. The two methyl groups were observed as two singlets at δ 1.137 and δ 1.132. Next, the reaction conditions were optimized and, for this, various reaction parameters were examined.



Scheme 2: Synthesis of Phthalazine derivatives by using nano-FGT

Firstly we focused on the optimization of amount of catalyst required to catalyze the reaction. It was discovered that 10 mg [6.32 mg of Fe, 11.31 mol%] of the catalyst was sufficient enough to furnish maximum yield within very short period of time. Application of higher amount of catalyst viz. 12 mg showed no increase in the yield of desired product, neither decreased reaction time. On the other hand, reduction in the amount of catalyst below 10 mg produced lower yield within same amount of time frame. The optimization plot of the reaction time and the catalyst is shown in Fig. 6.

Encouraged by the above success, we investigated the effect of various solvents on the pilot reaction at 80 ^0C using 10 mg nano-FGT as a catalyst. In presence of solvents like water, ethanol, acetonitrile and THF, bis-adduct **15a′**, 2,2′-(4-chlorophenylmethylene)- bis(3 hydroxy-5,5-dimethylcyclohex-2-enone), (see **SI**) was the major product instead of phthalazine derivative **15a**. But under solvent free condition, reaction proceeded very smoothly and offered phthalazine derivative **15a** as major product within very short period of time (Fig. 7).

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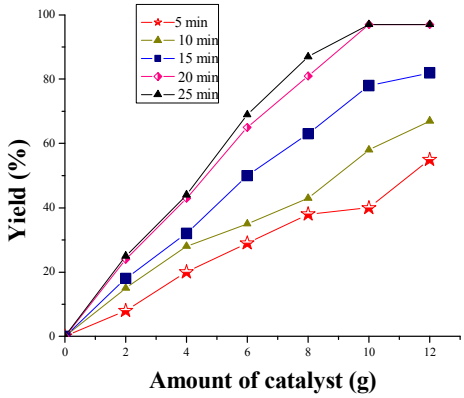

Fig. 6: Optimization of catalyst loading with respect to yield and time

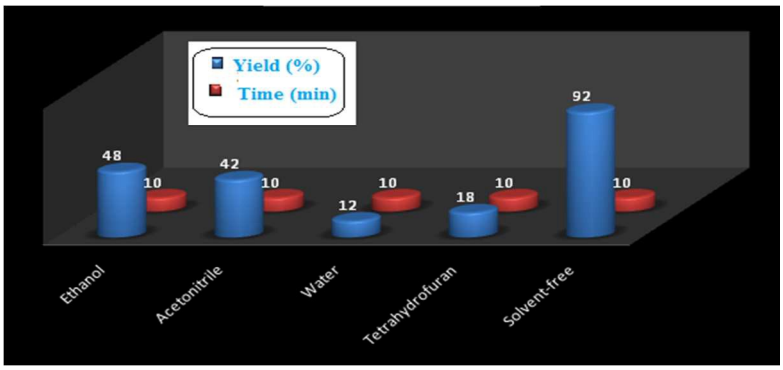

Fig. 7: Solvent standardization

Now in order to render the catalytic activity of nano-FGT in the above reaction as the best, we compared its catalytic activity with other homogeneous and heterogeneous catalysts. The cases where $FeCl_3$, Fe_2SO_4 and Fe_3O_4 NPs were used as catalyst witnessed very less conversion thereby leading to the poor yield of the desired product (Table 1). The fourth case where glutathione was used as the catalyst showed very good improvement in result but the time required for the completion of the reaction was high and in this case glutathione being soluble in water could not be recycled back. Application of nano-FGT however solved this problem of recyclability and since it is attached to nanoparticles which have higher surface/ volume ratios and it leads to better catalytic activity,[9] which in turn reduced the time and increase the product yield.

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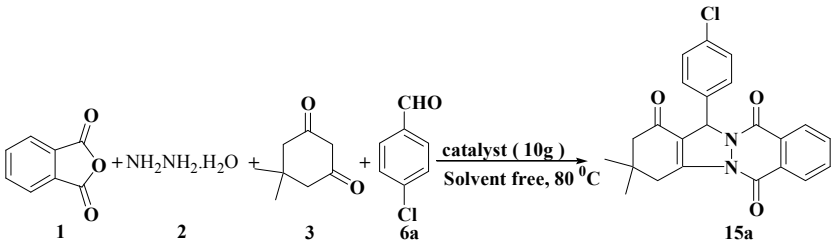
Table 1: Standardization of catalyst [a]



Scheme 3: Catalyst Screening

Sl.No.	Catalyst [b]	Time	Yield [c] (%)
1	No catalyst	24 h	0
2	$FeCl_3$	180 min	21
3	Fe_2SO_4	180 min	25
4	Fe_3O_4 NPs	180 min	53
5	Glutathione	120 min	78
6	Nano-FGT	20 min	97

[a] Reaction Condition : phthalic anhydride (1 mmol), hydrazinium hydroxide (1.2 mmol), dimedone (1 mmol) and 4-chlorobenzaldehyde (1 mmol), 80 ^{0}C, SFRC. [b] amount of catalyst: 10 mg. [c] isolated yield.

To explore generality of the reaction, we extended the scope of the present protocol for the synthesis of various phthalazine derivatives. The results of this study are shown in **Table 2**. As shown in the **Table 2,** aromatic aldehydes carrying either electron donating or withdrawing substituent worked well, giving excellent yield of products (87-97 %) with high purity. The reaction went smoothly with various active methylene compounds like dimedone (**3**), 1,3-cyclohexanedione (**4**), ethyl cyanoacetate (**5a**), and malononitrile (**5b**). To analyze the ability of our methodology, the said synthesis was also performed with different heteroaromatic and aliphatic aldehydes (**15o**, **15p** and **18a**) under similar conditions and we were delighted to see the formation of our desired product in good yields within similar time duration. As per as literature survey very less reported procedure for the synthesis of phthalazine derivatives showed good results with aliphatic and heteroaromatic aldehydes, but our methodology provides excellent results with both kinds of aldehydes **(Table 2).** Reaction was also tried with ethyl acetoacetate as active methylene compound but no desired product formed after 6 h of constant stirring only starting materials were recovered. All the syntheized products were characterized from their

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analytical and spectroscopic data. Structure of **compound 17a** was again confirmed by single X-ray crystallography (Fig. 8).

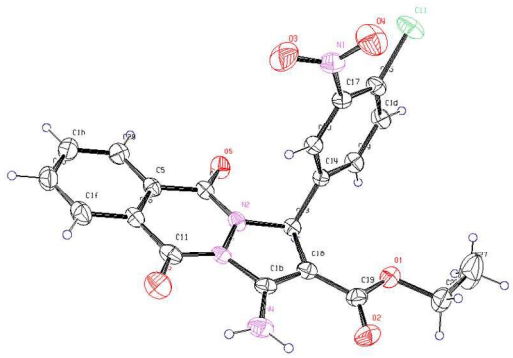
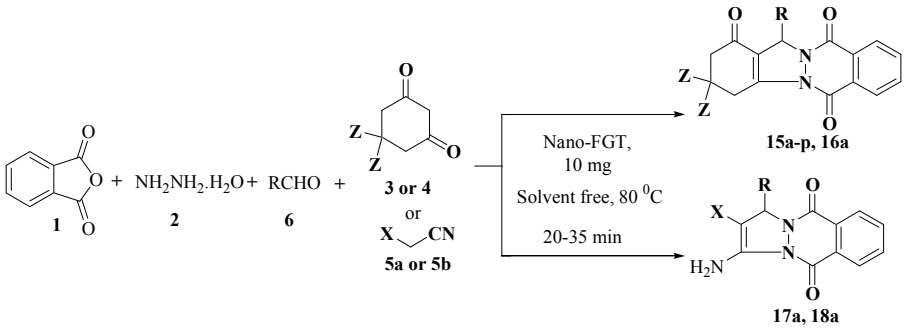


Fig.8: Molecular structure of compound 17a CCDC 1438715.

Table 2: Synthesis of various phthalazine derivatives by using nano-FGT.



If Z= -CH_3, 3;If Z= -H,4

If X= -COOEt, 5a;
If X= -CN, 5b;

R= Various aromatic, alliphatic and heteroaromatic aldehydes.

Scheme 4: Synthesis of Phthalazine derivatives

Sl. No.	Aldehydes	Active methylene compounds	Product	Time (min)	Yield (%) [b]	M.P. (^{0} C)
1	4-ClC_6H_5 (6a)	3	15a	20	97	261-262[17]
2	4-CNC_6H_5 (6b)	3	15b	20	96	271-273[25]
3	4-$NO_2C_6H_5$(6c)	3	15c	20	97	224-226[17]
4	4-BrC_6H_5(6d)	3	15d	25	96	265-267[17]
5	4-FC_6H_5(6e)	3	15e	20	95	219-220[17]
6	3-ClC_6H_5(6f)	3	15f	20	92	205-207[25]
7	2-ClC_6H_5 (6g)	3	15g	23	91	266-268[17]

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8	3- $NO_2C_6H_5$ (6h)	3	15h	24	92	269-270[25]
9	3-BrC_6H_5 (6i)	3	15i	21	92	266-268[25]
10	3-FC_6H_5 (6j)	3	15j	21	90	271-273[25]
11	2-BrC_6H_5 (6k)	3	15k	22	91	262-265[25]
12	C_6H_5 (6l)	3	15l	25	93	205-207[17]
13	4-MeC_6H_5 (6m)	3	15m	25	87	228-230[17]
14	4-$MeOC_6H_5$ (6n)	3	15n	20	89	220-222[25]
15	2-C_5NH_4 (6o)	3	15o	30	88	227-230[24]
16	C_4H_8 (6p)	3	15p	30	87	133-136[22]
17	4-$NO_2C_6H_5$(6c)	4	16a	20	94	237-239
18	4-Cl,3-$NO_2C_6H_5$ (6q)	5a	17aa	20	97	212-214
19	C_4H_8 (6p)	5b	18a	25	92	220-223

[a] Reaction Condition : phthalic anhydride (1 mmol), hydrazinium hydroxide (1.2 mmol), active methylene compounds (1 mmol) and aldehydes (1 mmol), 80 ^{0}C, SFRC,10 mg of nano-FGT. [b] isolated yield.

Most probable mechanism of the said conversion is shown in Scheme 5. In the initial step nano-FGT facilitates the nucleophilic attack of hydrazinium hydroxide (**2**) to phthalic anhydride (**1**) leading to the formation of phthalhydrazide (**7**). On the other hand, aldehydes reacts with nano-FGT forming imminium intermediate (**8**).[9] Then cyclic 1,3-diketones (**3** and **4**) forms **9** which reacts with **8** and afforded knoevenagel product **11** (path a)[9] where acyclic active methylene compounds (**5a** or **5b)** generates knoevenagel product **12** through carbanion formation (path b).[29] Phthalhydrazide (**7**) attacks these intermediates (**11** and **12**) under Michael fashion leading to the formation of other intermediates **13** and **14** which eventually undergoes cyclization followed by dehydration to furnish our desired product.

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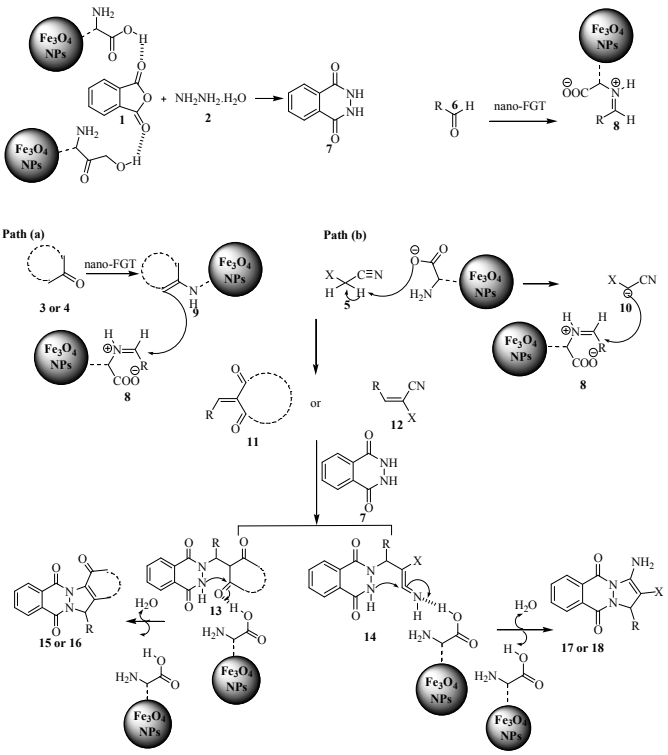

Scheme 5: Plausible mechanism for the synthesis of 2*H*-indazolo[1,2-*b*]phthalazine-triones and 1*H*-pyrazolo[1,2-*b*]phthalazine-diones.

Following this, the possibility of recovery and reusability of the catalyst was investigated. After completion of the reaction, the catalyst was recovered from the reaction mixture simply by using an external magnet and washed with ethylacetate, acetone and dried. The recovered catalyst was reused under same reaction condition and it was found that the catalyst could be reused for five times without any significant loss of the product yield. The reproducibility of the reaction was then investigated by performing five sets of reaction under same condition. Each set was repeated five times and mean of yield was calculated (95.6, 94.8, 94.2, 93.2 and 92.6 %) by standard deviation method, the error bars were also reported (Fig. 9). After carrying out 5th set of reaction, again ICP-OES analysis was performed and amount of Fe found was 60.04%, this observation confirmed there is 3.19% leaching of the catalyst. Then in order to confirm the structure of the reused (after 5 consecutive runs) catalyst we performed powder XRD (Fig. 10a), SEM (Fig. 10b), TEM (Fig. 10c), FT-IR (Fig. SI 1b) and TGA (Fig. 10d) analysis which were

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very similar to that of freshly synthesized catalyst and it also remained well dispersed and retained the size (10-20 nm).

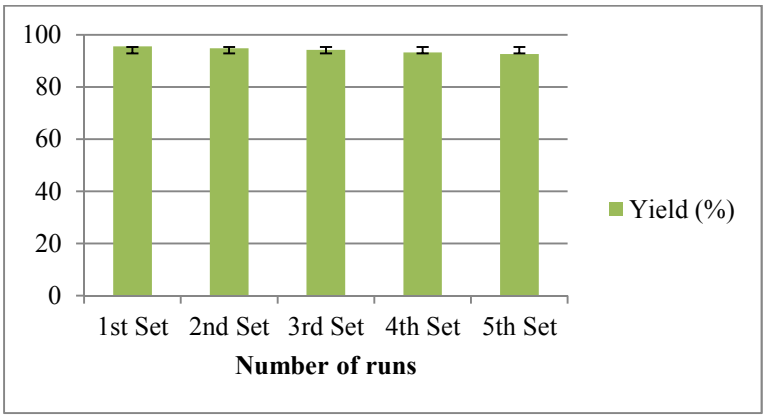
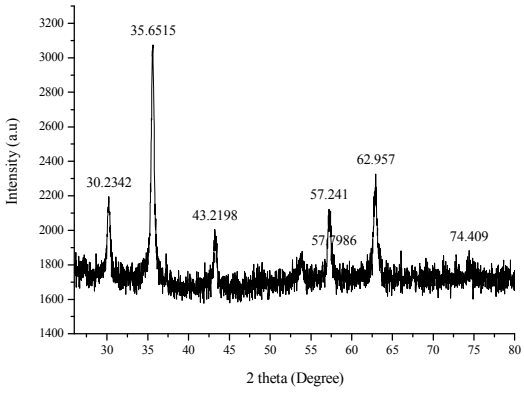


Fig. 9: Reproducibility chart



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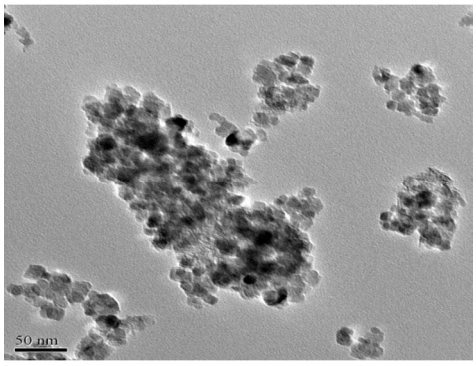

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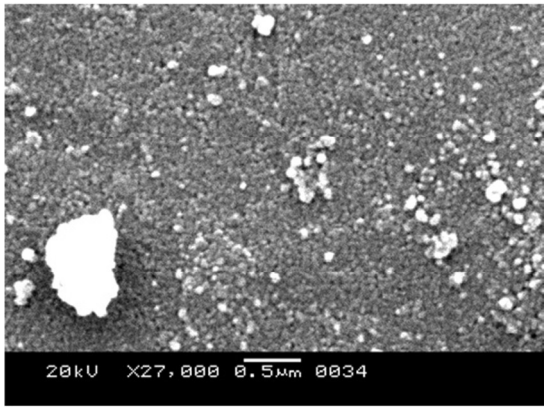
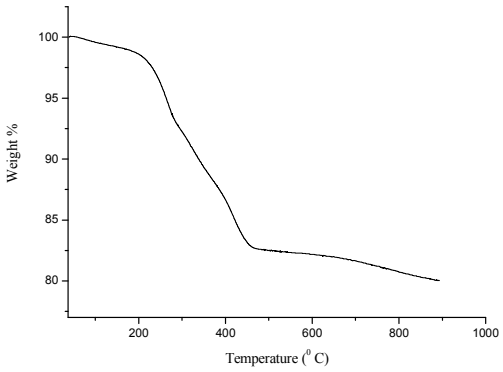


(c)



(d)

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Fig. 10: (a) powder XRD, (b)TEM image of nano-FGT at 50 nm, (C) SEM image of nano-FGT at 500 nm and (d) TGA curve of nano-FGT after 5th run.

Conclusion:

In conclusion, herein we report a stable nano-organocatalyst mediated solvent free one-pot synthesis of 2*H*-indazolo[2,1-*b*] phthalazine-trione derivatives and 1H-pyrazolo[1,2-*b*] phthalazine-dione derivatives within short period of time. The reaction went smoothly with various active methylene compounds and also with diverse range of aldehydes (aromatic, aliphatic and heteroaromatic) showing the versatility of the methodology. After completion of the reaction Nano-FGT was easily recovered from the reaction mixture by a simple and convenient magnetic separation using an external magnet. This methodology also overcomes the formation of by product, low yields, use of toxic catalyst and hazardous organic solvent. Moreover, catalyst can be recycled and reused up to five consecutive run without much decrease in catalytic activity.

Experimental:

Phthalic anhydride (1 mmol) (**1**), hydrazinium hydroxide (1.2 mmol) (**2**), active methylene compounds (1 mmol) (**3/4/5**), aryl aldehydes (1 mmol) (**6a-q**) and nano-FGT (10 mg) were added to a round bottom flask and since the reaction is under solvent free condition so it was mixed properly by using a glass rod. Following this, a magnetic bit was added and the reaction mixture was set on a pre-heated oil bath at 80 ^{0}C accompanied with magnetic stirrer (model no: IKA C-MAG, HS4 Digital) and stirring was started and continued for the time mentioned in the **Table 2**. During stirring a centrifugal force was generated, which mixed the reactants nicely thereby making a reasonable contact between the surface of the catalyst and the reactants. This fact was clearly explained from the observation that when no catalyst was added to the reaction mixture, no desired product was formed even after 24 h of stirring. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature. 10 mL of ethyl acetate was added to the reaction mixture and nano-FGT attached to magnetic bit was separated by another external magnet. After that, in order to reuse the catalyst, it was washed several times with ethyl acetate, acetone to remove presence of any residual product and dried. The catalyst was then applied in subsequent reactions. The organic extract was then washed with water (3x10 ml), followed by brine and dried with anhydrous Na_2SO_4. The solvent was removed

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under vacuum and the crude reaction mixture was purified by column chromatography using ethyl acetate: hexane (4:6) to afford the pure products (**15a-p, 16a, 17a, 18a**).

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