Boric Acid Supported on Montmorillonites as Catalysts for Synthesis of 2,3-dihydroquinazolin-4(*1H*)-ones

Kancherla, Mahesh
Department of Chemistry, Vel Tech High Tech Dr. Rangarajan Dr. Sakunthala Engineering College, Avadi, Chennai-600 062, INDIA

Katlakanti, Mohan Reddy
Department of Chemistry, College of Engineering Studies, University of Petroleum & Energy Studies (UPES), Bidholi Campus, Dehradun-248 007, INDIA

Seku, Kondaiah
Department of Chemistry, Shinas College of Technology, Shinas, OMAN

Badathala, Vijayakumar*+
Department of Chemistry, Vel Tech High Tech Dr. Rangarajan Dr. Sakunthala Engineering College, Avadi, Chennai-600 062, INDIA

ABSTRACT: *Synthesis of 2,3-dihydroquinazolin-4(1H)-ones using H_3BO_3/montmorillonite K10 (H_3BO_3/mont K10) catalyst has been reported. H_3BO_3/mont K10 and H_3BO_3/mont K30 have been prepared and used as catalysts in the reaction between anthranilamide and benzaldehyde to prepare 2-phenyl-2,3-dihydroquinazolin-4(1H)-one. The catalysts have been characterized for their physico-chemical properties by XRD, IR, BET surface analysis, TGA, SEM, and DRIFTS. H_3BO_3/mont K10 has shown better catalytic activity among the catalysts tested for the synthesis of 2-phenyl-2,3-dihydroquinazolin-4(1H)-one. The reaction conditions have been optimized for 2-phenyl-2,3-dihydroquinazolin-4(1H)-one and the reusability of H_3BO_3/mont K10 has also been investigated. Several 2,3-dihydroquinazolin-4(1H)-one derivatives have been synthesized in good to excellent yields using the optimized reaction conditions.*

KEYWORDS: *Clays; catalysts; H_3BO_3/mont K10; H_3BO_3/mont K30; 2,3-dihydroquinazolin-4(1H)-ones.*

INTRODUCTION

Clays are hydrous layered silicates and occur easily in nature. Clays have been used as catalysts for various organic transformations. Because of their simple modification procedures, lower cost, recyclability,

** To whom correspondence should be addressed.*
+ E-mail: badathala@yahoo.com
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and environmentally friendly nature, lot of attention is drawn in developing novel methods of using clays as catalysts for variety of organic reactions [1].

Quinazolinone derivatives are a class of compounds that are present in several bioactive natural products and pharmaceutical compounds. Particularly, 2,3-dihydroquinazolinone derivatives possess many biological, medicinal and pharmacological properties exhibiting antibiotic, anticancer, antidepressant, antihistamine, antihypertonic, antipyretic, antitumor, antituberclosis, analgesic, diuretic, and vasodilating activities [2-6]. The potential biological and pharmaceutical activities of quinazolinones have driven researchers to develop new methods for their synthesis.

From the literature, many synthetic methods have been disclosed for the synthesis of 2,3-dihydroquinazolinones and the most of the methods include cyclocondensation reaction of isatoic anhydride, aromatic aldehydes and primary amines or ammonium salts and condensation of aryl, alkyl, and heteroaryl aldehydes with anthranilamide in presence of catalysts. Synthesis of 2,3-dihydroquinazolinone derivatives has been accomplished by using HCl [7], *p*-TSA/$NaHSO_3$ [8], SmI_2[9], $TiCl_4$ [10], $CuCl_2$ [11], $KAl(SO_4)_2{\cdot}12H_2O$ [12], $SnCl_2$ [13], Montmorillonite K10 [14], Amberlyst-15 [15], ionic liquids [16], molecular iodine [17], ammonium chloride [18], gallium(III) triflate [19], silica sulfuric acid [20], trifluoroacetic acid [21], [bmim]HSO_4[22], $ZnCl_2$ [23], cellulose-SO_3H [24], sulfamic acid [25], thiamine hydrochloride [26], cyanuric acid [27], β-cyclodextrin [28], 2-morpholinoethanesulfonic acid [29], polyethylene glycol-400 [30], iron(III) chloride [31], K_3PO_4 [32], Pt-MWCNT [33], $LaCl_3$/nano SiO_2 [34], $Y(OTf)_3$ [35], *p*-sulfonic acid calix[4]arene [36], Fe_3O_4-SA-PPCA [37], hydroxyapatite nanoparticles [38], nickel complex anchored onto MCM-41 [39], lactic acid [40], molecular sieve supported lanthanum [41], graphene oxide nano sheets [42], *N*-sulfonic acid pyridinium chloride [43], and α-chymotrypsin [44].

Some methods described in the literature for synthesis of 2,3-dihydroquinazolinone derivatives have disadvantages and few catalysts have disposal problems after use, and they also have the drawbacks with respect to reaction time, cost of the reagents or catalysts, purity of products, tedious reaction workups, etc., for example, transition metal salts and ionic liquids are expensive and mineral acids are corrosive. Hence, the development of a convenient, efficient, and environmentally friendly method is needed to prepare 2,3-dihydroquinazolinones.

In continuation of our research on the development of clay catalysts for organic transformations [45, 46], herein we report a simple and environmentally benign method for the synthesis of 2,3-dihydroquinazolin-4(*1H*)-ones in the presence of H_3BO_3/mont K10.

EXPERIMENTAL SECTION

Materials

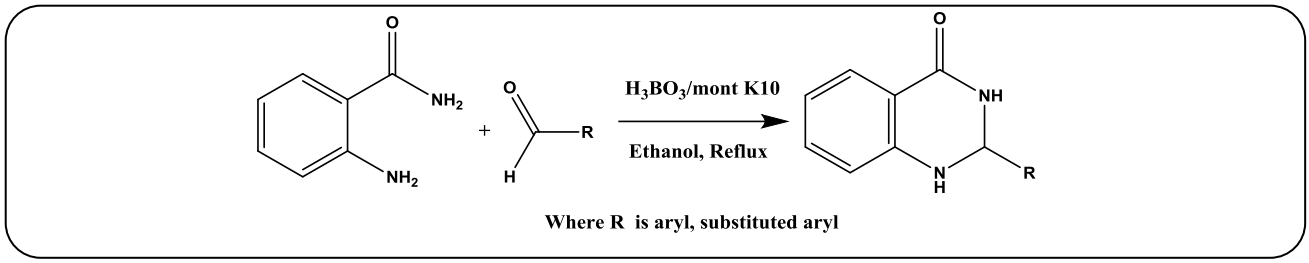
Montmorillonite K10 (Mont K10), Montmorillonite K30 (Mont K30), and Montmorillonite KSF (Mont KSF) catalysts have been procured from Sigma-Aldrich. The reagents were purchased from Avra synthesis, E-Merk, Qualigens, and Loba Chemie, India. The reagents were used as-received and some of them were purified by distillation.

Preparation of catalysts: Procedure for preparation of H_3BO_3/mont K10 and H_3BO_3/mont K30

2 g of boric acid (H_3BO_3) and 10 g Mont K10 were weighed accurately. The measured boric acid was dissolved in 70 mL of deionised water. The H_3BO_3 solution was loaded on the measured quantity of Mont K10 with constant stirring in a 250 mL round bottom flask and refluxed for 4 h. The round bottom flask was cooled to room temperature, water was evaporated under vacuum, and the resultant material was dried in an oven at 100 °C for 3 h to obtain H_3BO_3/mont K10. Similarly, H_3BO_3/mont K30 was also prepared.

General procedure for the preparation of 2,3-dihydroquinazolin-4(1H)-ones (Scheme 1)

A mixture of anthranilamide (1 mmol) and aldehyde (1.2 or 1.5 mmol) was refluxed with H_3BO_3/mont K10 (100 mg) in ethanol (10 mL) medium at appropriate time. The reaction mixture was cooled to room temperature and filtered off to isolate the catalyst. The excess solvent from the reaction mixture was removed under vacuum; the resultant solid was dissolved in dichloromethane (15 mL), and scrubbed with water (10 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum to obtain crude product. Finally, the crude product was recrystallized from ethanol to afford pure corresponding 2,3-dihydroquinazolin-4(*1H*)-one. The purified products were identified by their melting points, ^{1}H NMR, and IR spectra.



Scheme 1: Preparation of 2,3-dihydroquinazolin-4(1H)-ones catalyzed by H_3BO_3/mont K10.

Characterization

Powder X-Ray Diffraction (PXRD) data were collected on Rigaku XPert Pro X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm). The InfraRed (IR) spectra have run between the ranges of 450-4000 cm^{-1} on JASCO 4600 FT-IR spectrometer by applying KBr pellet method. The specific surface areas of the samples were investigated by Brunauer-Emmett-Teller (BET) method using N_2 adsorption-desorption at 77 K on Micromeritics ASAP 2020 surface area analyzer and the porosity distribution was collected from the adsorption branch of the isotherm using Barrett-Joyner-Halenda (BJH) analysis. The samples were out gassed at 150 °C for 12 h before physisorption measurements. The ThermoGravimetry (TG) analysis has collected on a TA SDT Q600 instrument in N_2 (50 mL/min) with a heating rate of 10 °C/min from ambient temperature to 800 °C. The SEM analysis of sample powders was recorded on an FE-SEM (SERON Technology, Korea). Acidity of solid catalysts was measured using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) by pyridine using a JASCO 4600 FT-IR spectrometer with DRIFTS accessory [46, 47]. The ^1H NMR spectra were collected on Bruker 300 MHz and/or Bruker 400 MHz (Avance III HD) spectrometer. Melting points of 2,3-dihydroquinazolin-4(*1H*)-ones were identified by using an electro thermal melting point apparatus in open capillaries and were uncorrected.

RESULTS AND DISCUSSION

PXRD Analysis

Fig. 1 shows XRD patterns of Mont K10, H_3BO_3/mont K10, Mont K30, and H_3BO_3/mont K30. The XRD patterns of Mont K10 and Mont K30 (Monts) have shown smectite (Sm), feldspar (F) and quartz (Q). The monts have 2θ values at 8.86, 17.67, 19.83, 20.70, 26.62, 27.63, 29.80, 35.09, and 45.53. The intensity of the peaks has increased in the boric acid supported monts due to better dispersion of boric acid on the monts which also indicates no change in the structure of the parent monts after simple modification.

FT-IR Analysis

Fig. 2 shows infrared spectra of H_3BO_3, Mont K10, Mont K30, H_3BO_3/Mont K10 and H_3BO_3/Mont K30. Boric acid has shown infrared band at 3217 cm^{-1} for O-H stretching , 1466 cm^{-1} for asymmetric stretching vibrations of B-O, 1193 cm^{-1} for B-O-H in plane bending, 886 cm^{-1} for symmetric stretching vibrations of B-O, 814 cm^{-1} for B-O-H out of plane bending, 646 cm^{-1} for deformation vibration of atoms in B-O, and 550 cm^{-1} for B-O-B vibration [48]. Infrared bands at 3435 and 1639 cm^{-1} were observed in all the monts, due to the stretching and bending vibrations of water molecules or hydroxyl groups in the interlayer. A band at about 3634 cm^{-1} assigned to lattice hydroxyls O-H stretching mode which arise from the vibration of firmly bound H_2O. The shoulder band near 1124 cm^{-1} is assigned to the Si–O bending vibration, while the Si–O–Si stretching vibration has appeared near 1036 cm^{-1} as a strong band. The shoulder band at 916 cm^{-1} can be attributed to Al–OH group and the band near 797 cm^{-1} is due to the skeletal vibrations of quartz [49]. The band at 1466 cm^{-1} in boric acid has shifted to 1419 cm^{-1} in H_3BO_3/monts. Further, many bands in boric acid have merged with bands of monts in H_3BO_3/monts.

Surface Characteristics

BET surface areas and pore-size distributions (adsorption branch) have been calculated for the monts and the values are shown in Table 1. H_3BO_3/Mont K10, and H_3BO_3/Mont K30 have shown reduced specific surface areas compared to their patent monts due to dispersion of boric acid on monts.

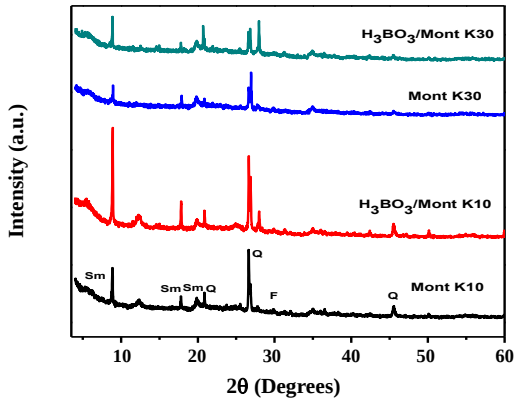


Fig. 1: PXRD patterns of Mont K10, H_3BO_3/mont K10, Mont K30, and H_3BO_3/mont K30.

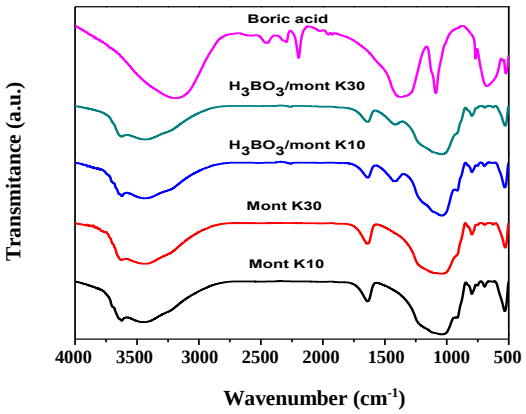


Fig. 2: IR spectra of Mont K10, H_3BO_3/mont K10, Mont K30, and H_3BO_3/mont K30.

Fig. 3 shows nitrogen adsorption-desorption isotherms of Mont K10, H_3BO_3/Mont K10, Mont K30, and H_3BO_3/mont K30. The parent monts exhibit well defined hysteresis loops in the relative pressure (P/P_o) range of 0.40 to 0.99, whereas boric acid supported monts exhibit hysteresis loops in the relative pressure (P/P_o) range of 0.43 to 0.99. Mont K10 and its modified form exhibit slightly bigger hysteresis loops compared to Mont K30 and its modified form in the relative pressure (P/P_o) range of 0.40 to 0.99. The sorption isotherms of catalysts are of type IV (H3) which indicates the presence of mesoporous slit-shaped pores [50]. Fig. 4 shows the BJH pore-size distribution curves for Mont K10, H_3BO_3/Mont K10, Mont K30, and H_3BO_3/mont K30. The Mont K10, Mont K30 and their modified forms possess mesopores. H_3BO_3/Mont K10 and H_3BO_3/Mont K30 have shown reduced pore diameters due to dispersion of boric acid into the pores of parent monts and therefore they have shown reduced surface areas.

TG Analysis

Fig. 5 shows TG profiles of Mont K10, Mont K30, H_3BO_3/Mont K10, and H_3BO_3/Mont K10. The TG profiles of monts and H_3BO_3/monts show an initial sharp decrease due to the loss of physically adsorbed water and interlayer water in monts and a second one beyond about 120–400 °C due to dehydration of boric acid [51] and the gradual loss of the hydroxyl groups in monts. The loss at 400–550 °C is hydroxyl water associated with their structure. Between 550 and 700 °C, an additional amount of water is lost [52]. There is a negligible weight loss beyond 700 °C in all catalysts. H_3BO_3/monts have shown more weight loss compared to their parents due to dehydration of boric acid present on them.

SEM Analysis

The surface distribution morphology of Mont K10, Mont K30, H_3BO_3/mont K10, and H_3BO_3/Mont K30 is demonstrated in Fig. 6. It is evident from the SEM pictures that both the parent monts and their modified forms have particles of different shapes and sizes. However, H_3BO_3/monts have many smaller size particles or platelets due to treatment with boric acid.

DRIFTS Studies

The acidity of the monts has been investigated by DRIFTS using pyridine as a probe molecule. Pyridine has been used as a probe molecule for the determination of the nature of acid sites on the surface of solid catalysts, particularly clay catalysts [53]. The DRIFTS spectra of Mont K10, Mont K30, H_3BO_3/Mont K10, and H_3BO_3/Mont K30 after pyridine adsorption are shown in Fig. 7. In this study, the infrared bands are observed at 1545, 1490, and 1443 cm^{-1} for the monts. Further, hydrogen-bonded pyridine typically absorbs at 1440 and 1490 cm^{-1}. The vibrations at 1443 cm^{-1} are associated with pyridine coordinated to Lewis sites, the vibrations at 1545 cm^{-1} are associated to pyridine bound to Brønsted sites (pyridinium ions), and the vibrations at 1490 cm^{-1} are associated to pyridine bound to both Brønsted and Lewis acid sites [47]. It is evident that the acidity of monts has increased after modification. The acid sites

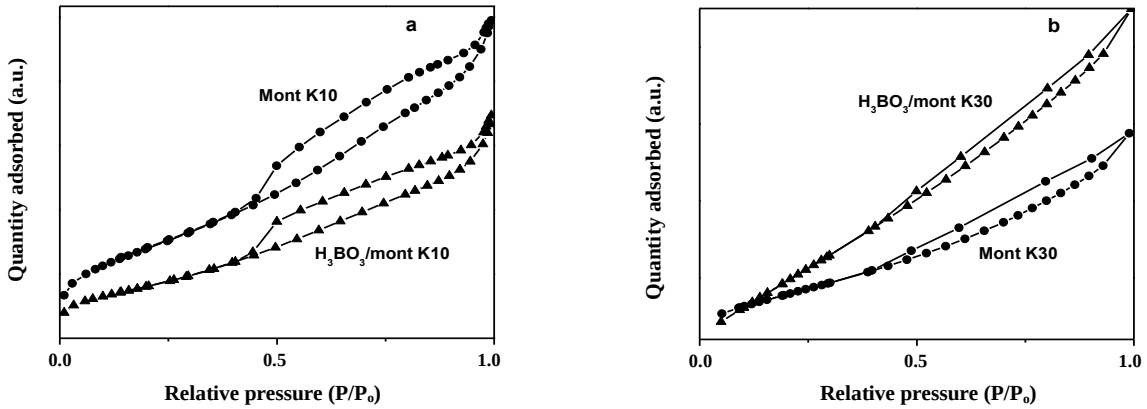


Fig. 3: Nitrogen adsorption-desorption isotherms of a) Mont K10, and H_3BO_3/mont K10, b) Mont K30, and H_3BO_3/mont K30.

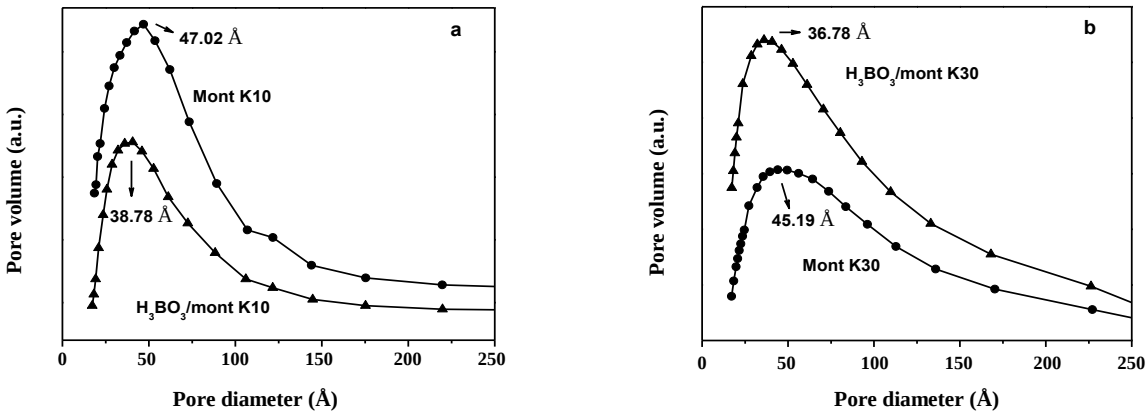


Fig. 4: BJH pore size distribution curves of a) Mont K10, and H_3BO_3/mont K10, b) Mont K30, and H_3BO_3/mont K30.

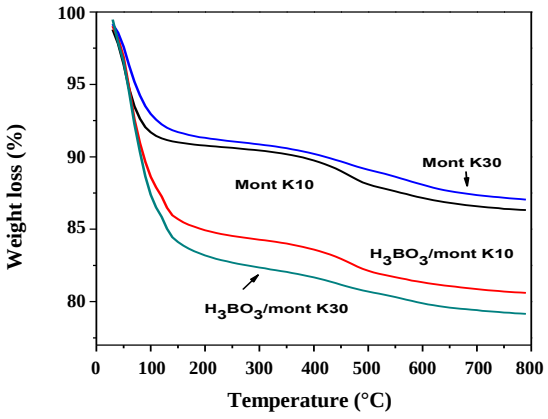


Fig. 5: Thermo gravimetric profiles of Mont K10, H_3BO_3/mont K10, Mont K30, and H_3BO_3/mont K30.

(at 1545 cm^{-1} & 1490 cm^{-1}) in H_3BO_3/mont K10 and H_3BO_3/Mont K30 are more over Mont K10 and Mont K30 respectively. Further, all the monts have shown Brønsted and Lewis acid sites. Mont KSF has shown better acidity (c in Fig. 7). The band at 1443 cm^{-1} in H_3BO_3/Mont K30 has merged with the band for hydrogen-bonded pyridine.

Catalytic Activity

The activity of the catalysts was tested on the reaction between anthranilamide and benzaldehyde in ethanol. The percentage yields of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one were obtained in different reactions carried out using different catalysts are presented in Table 1. The activity under specified conditions as summarized in Table 1, is as follows: H_3BO_3 > H_3BO_3/Mont K10 > H_3BO_3/Mont K30 > Mont K10 > *p*-TSA > Mont KSF > Mont K30 > No catalyst. It is to be noted that though boric acid catalyzed reaction yields 75% of the product, the catalyst cannot be reused. The activity of the catalysts for the reaction between anthranilamide and benzaldehyde in ethanol has been correlated with the data of acid sites obtained from DRIFTS study using pyridine. The activity of the catalysts is found to follow

Table 1: Activity of catalysts for the reaction between anthranilamide and benzaldehyde.

Entry	Catalyst	Sp. Surface area (m^2/g)	Avg. pore diameter (Å)	Yield (%)*
1	Mont K10	155	47.02	41
2	Mont K30	138	45.19	26
3	Mont KSF	5	--	31
4	H_3BO_3/mont K10	89	38.78	67
5	H_3BO_3/mont K30	78	36.78	45
6	*p*-TSA	--	--	36
7	H_3BO_3	--	--	75
8	No catalyst	--	--	Nil

** Isolated yield. Reaction conditions: Molar ratio (Anthranilamide: benzaldehyde): 1:1.2; Amount of catalyst: 100 mg; Solvent: Ethanol; Time: 4 h.*

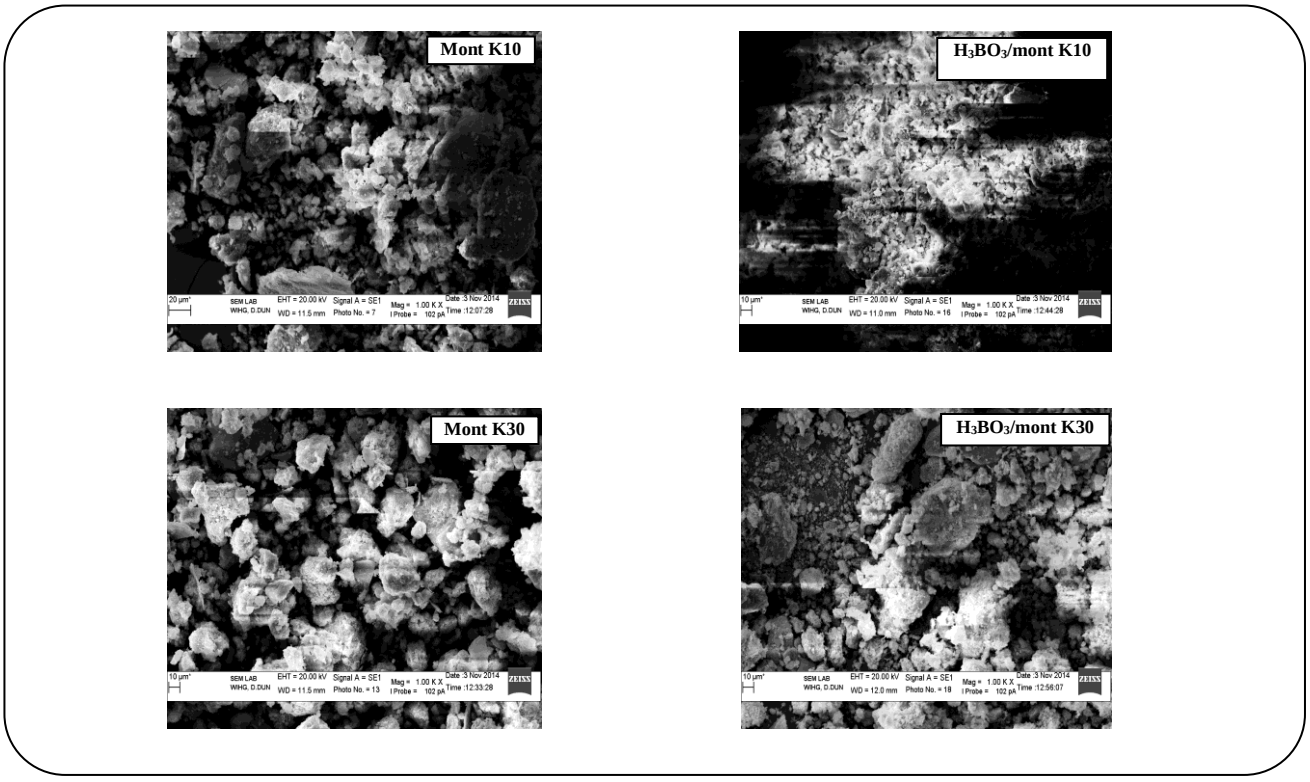


Fig. 6: SEM images of Mont K10, H_3BO_3/mont K10, Mont K30, and H_3BO_3/mont K30.

the sequence: H_3BO_3/Mont K10 > H_3BO_3/Mont K30 > Mont K10 > Mont K30, which is in agreement with their Brønsted acidity data. It is clear from the results that H_3BO_3/monts having lower surface area and pore diameter than their parent monts have shown better acidity and activity. However, Mont KSF, with the lowest surface area of the monts tested, has shown better acidity in DRIFTS. It can be concluded that the activity of catalysts depends on acidity, surface characteristics, accessibility of acidic sites, nature of the reactants, and solvent.

H_3BO_3/Mont K10 and H_3BO_3/Mont K30 have been used as catalysts for the reaction between anthranilamide and benzaldehyde and the effects of different parameters such as solvent, molar ratio, amount of catalyst, and time on the yield of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one have been studied. Further, some 2,3-dihydroquinazolin -4(*1H*)-one derivatives have been synthesised

Table 2: Effect of solvent on the yield of 2-phenyl-2,3-dihydroquinazolin-4(1H)-one.

Entry	Solvent (b.p.)	Yield (%)* with H_3BO_3/mont K10	Yield (%)* with H_3BO_3/mont K30
1	Methanol (64.7 °C)	13	39
2	Ethanol (78 °C)	67	45
3	Water (100 °C)	Nil	Nil
4	Toluene (110 °C)	11	51
5	o-Xylene (142 °C)	32	41

** Isolated yield. Reaction conditions: Molar ratio (Anthranilamide: benzaldehyde): 1:1.2; Amount of catalyst: 100 mg; Time: 4 h.*

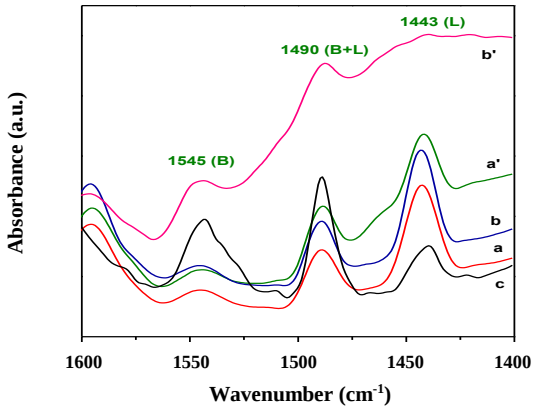


Fig. 7: DRIFTS spectra of a) Mont K10, a') H_3BO_3/Mont K10, b) Mont K30, b') H_3BO_3/mont K30, and c) Mont KSF after pyridine adsorption.

using the optimised conditions and reusability of H_3BO_3/mont K10 has been investigated.

The reaction between anthranilamide and benzaldehyde was carried out in five different solvents for four hours (Table 2). It was found that the reaction catalyzed by H_3BO_3/Mont K10 in ethanol yields maximum, 67% (entry 2, Table 2). However, there was no reaction in water (entry 3, Table 2) catalyzed by both catalysts. The reactions catalyzed by H_3BO_3/Mont K30 in different solvents yielded the product in 39-51%. It was also observed that the yields were not dependent on the boiling points of the solvents and further the yields were not appreciable in non-polar solvents such as toluene and *o*-xylene in presence of H_3BO_3/mont K10. Therefore, further reactions were studied in ethanol solvent.

Effect of Molar Ratio

The reaction between anthranilamide and benzaldehyde was carried out in presence of H_3BO_3/Mont K10 and H_3BO_3/Mont K30 using equimolar ratio of anthranilamide and benzaldehyde, wherein the 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one yield was lower (entry 1, Table 3). When the molar ratio of anthranilamide to benzaldehyde was gradually increased from 1:1 to 1: 3, in presence of the catalysts, higher quantities of the product were formed (Table 3). This shows that the reaction equilibrium shifts towards the formation of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one when benzaldehyde concentration was increased. However, the yield of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one was 91% when the anthranilamide to benzaldehyde ratio was 1:1.5 and there was a small improvement in the percentage yield of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one when the anthranilamide to benzaldehyde ratio was above 1:1.5 (Table 3) in presence of H_3BO_3/mont K10, whereas the percentage yield of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one was gradually increased till the anthranilamide to benzaldehyde ratio was 1:2.5 in H_3BO_3/Mont K30 catalyzed reaction. Hence, for studies on preparation of various 2,3-dihydroquinazolin-4(*1H*)-ones using H_3BO_3/mont K10, the anthranilamide to aldehyde ratio of 1:1.5 was selected.

Effect of Amount of Catalyst

The reaction between anthranilamide and benzaldehyde was carried out using 50 to 250 mg of the catalyst in ethanol solvent for four hours. The product yields were increased with increase in the catalyst amount as shown in Fig. 8. It is clear from the results that accessibility, the strength of the acidic sites, and their concentration are responsible for increased yields in this reaction. When 100-250 mg of H_3BO_3/ Mont K10 was used the yield of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one slightly decreased. On the other hand, the yield gradually increased till 200 mg of H_3BO_3/Mont K30 and thereafter it decreased.

Table 3: Effect of molar ratio on the yield of 2-phenyl-2,3-dihydroquinazolin-4(1H)-one.

Entry	Molar Ratio [Anthranilamide: benzaldehyde]	Yield (%)* with H_3BO_3/mont K10	Yield (%)* with H_3BO_3/mont K30
1	1:1	26	19
2	1:1.1	43	40
3	1:1.2	67	45
4	1:1.5	91	76
5	1:2	93	88
6	1:2.5	96	96
7	1:3	98	96

** Isolated yield. Reaction conditions: Amount of catalyst: 100 mg; Solvent: Ethanol; Time: 4 h.*

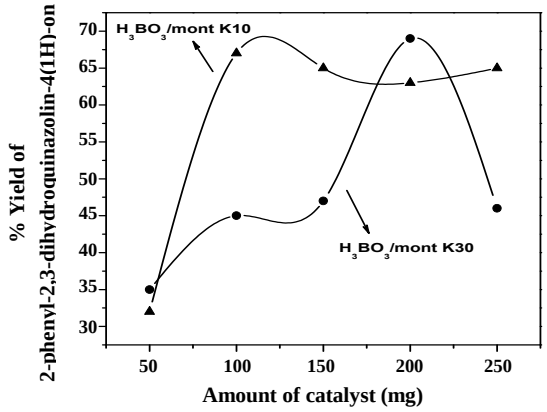


Fig. 8: Effect of catalyst amount on the yield of 2-phenyl-2,3-dihydroquinazolin-4(1H)-one. Reaction conditions: Molar ratio (Anthranilamide: benzaldehyde): 1:1.2; Amount of catalyst: 100 mg; Solvent: Ethanol; Time: 4 h

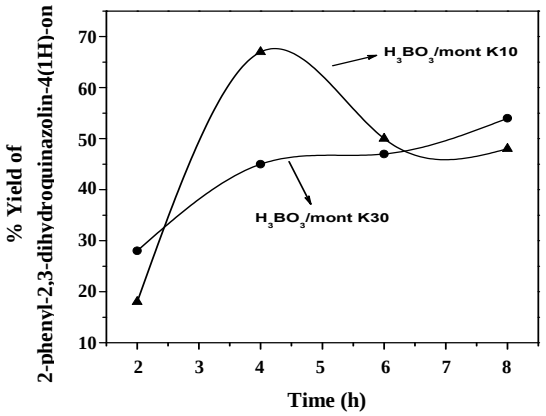


Fig. 9: Effect of time on the yield of 2-phenyl-2,3-dihydroquinazolin-4(1H)-one. Reaction conditions: Molar ratio (Anthranilamide: benzaldehyde): 1:1.2; Amount of catalyst: 100 mg; Solvent: Ethanol

In general, the reactions that are catalyzed by clays follow adsorption and diffusion of reactants through the pores and interlayers. The diffusion of the reactants in the active sites present on the catalyst becomes a limiting process in porous solid acid catalysts. Firstly, the reactants are adsorbed on the active sites of the catalyst and form products through formation of intermediate complex. The product formed comes out of the sites. If excess catalyst is used, even though more active sites are available, the product formed remains adsorbed within the active sites of the catalyst and restricts diffusion for the fresh reactants. Hence, the decrease in the yield of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one was observed due to unavailability of active sites to the reactants when excess catalysts were used. Therefore, 100 mg of H_3BO_3/Mont K10 was used for studies on preparation of various 2,3-dihydroquinazolin-4(*1H*)-ones.

Effect of Time

In order to study effect of time on the yield of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one, the reaction between anthranilamide and benzaldehyde has been studied at 2, 4, 6, and 8 hour intervals of time. Fig. 9 shows the effect of reaction time on the yield of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one for 1 mmol of anthranilamide, 1.2 mmol of benzaldehyde and 100 mg of H_3BO_3/Mont K10 and H_3BO_3/Mont K30. The yield of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one increased with increase in reaction time from 2 to 4 h. Further increase in the reaction time beyond 4 h resulted in reduced yield of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one in presence

Table 4: H_3BO_3/mont K10 catalyzed synthesis of various 2,3-dihydroquinazolin-4(1H)-one derivatives.

Entry	Aldehyde	Product	Yield (%)*	Melting point
1	Benzaldehyde	2-Phenyl-2,3-dihydroquinazolin-4(*1H*)-one	91	219-221 ˚C [16]
2	2-Chlorobenzaldehyde	2-(2-Chlorophenyl)-2,3-dihydroquinazolin-4(*1H*)-one	89	210-212 ˚C [54]
3	3-Chlorobenzaldehyde	2-(3-Chlorophenyl)-2,3-dihydroquinazolin-4(*1H*)-one	96	179-181 ˚C [55]
4	4-Chlorobenzaldehyde	2-(4-Chlorophenyl)-2,3-dihydroquinazolin-4(*1H*)-one	75	203-205 ˚C [25]
5	2-Hydroxybenzaldehyde	2-(2-Hydroxyphenyl)-2,3-dihydroquinazolin-4(*1H*)-one	59	222-224 ˚C [42]
6	4-Hydroxybenzaldehyde	2-(4-Hydroxyphenyl)-2,3-dihydroquinazolin-4(*1H*)-one	84	278-280 ˚C [54]
7	4-Methoxybenzaldehyde	2-(4-Methoxyphenyl)-2,3-dihydroquinazolin-4(*1H*)-one	94	189-191 ˚C [25]
8	2-Nitrobenzaldehyde	2-(2-Nitrophenyl)-2,3-dihydroquinazolin-4(*1H*)-one	78	183-185 ˚C [19]
9	3-Nitrobenzaldehyde	2-(3-Nitrophenyl)-2,3-dihydroquinazolin-4(*1H*)-one	85	209-211 ˚C [25]

** Isolated yield. Reaction conditions: Molar ratio (Anthranilamide: aldehyde): 1:1.5; Amount of catalyst, H_3BO_3/mont K10: 100 mg; Solvent: Ethanol; Time: 4 h.*

of H_3BO_3/mont K10. This phenomenon can be attributed to decomposition of unreacted reactants and/or product formed due to prolonged heating. However, the yield of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one was lower and increased with increase in reaction time from 2 to 8 h in presence of H_3BO_3/mont K30.

The reaction was found to follow first order kinetics with respect to anthranilamide in presence of H_3BO_3/mont K10. The rate constant, the equilibrium constant for maximum yield, and the standard free energy change, are found to be $\kappa=4.67\times10^{-5}$ s^{-1}, $K=4.58\times10^{6}$, and $\Delta G°= -44757$ J mol^{-1} respectively.

Synthesis of 2,3-Dihydroquinazolin-4(1H)-one Derivatives

To show the merit of the present investigation, the optimized reaction conditions were applied to the reaction of anthranilamide with several aldehydes. Table 4 shows the reaction of anthranilamide with various aldehydes. Among the aldehydes, benzaldehyde, 3-chloro, and 4-methoxy substituted benzaldehydes gave corresponding 2,3-dihydroquinazolin-4(1*H*)-ones in 91-96% yield, 4-hydroxy, 3-nitro, and 2-chloro substituted benzaldehydes gave corresponding 2,3dihydroquinazolin-4(1*H*)-ones in 84-89% yield, 4-chloro, and 2-nitro substituted benzaldehydes gave corresponding 2, 3-dihydroquinazolin-4(1*H*)-ones in 75 and 78% yield respectively, whereas 2-hydroxybenzaldehyde gave corresponding 2, 3-dihydroquinazolin-4(1*H*)-ones in 59% yield (entry 8, Table 4) due to retarding effect towards product formation.

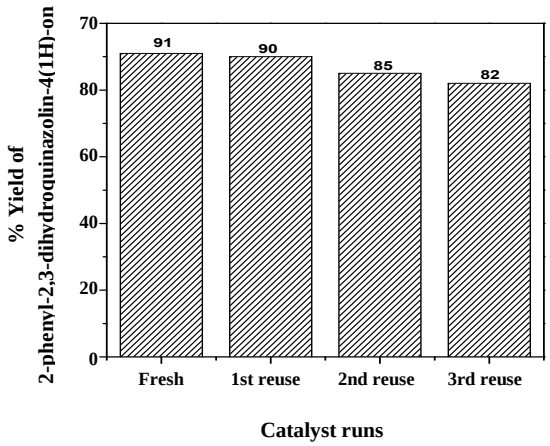


Fig. 10: Recyclability of H_3BO_3/mont K10. Reaction conditions: Molar ratio (Anthranilamide: benzaldehyde): 1:1.5; Solvent: Ethanol; Time: 4 h

Regeneration and Reuse of H_3BO_3/mont K10

The used catalyst was washed with DCM and activated at 110 °C for 2 h. The regenerated catalyst was used for preparing 2-phenyl-2, 3-dihydroquinazolin-4(*1H*)-one and observed about 9% loss in its activity at 3rd reuse (Fig. 10).

CONCLUSIONS

Environmentally friendly mild H_3BO_3/montmorillonite catalysts have been prepared, characterized, and used them for efficient synthesis of 2-phenyl-2,3-dihydroquinazolin-4(*1H*)-one by optimizing the reaction conditions. Several 2,3-dihydroquinazolin-4(*1H*)-one

derivatives have been synthesized using H_3BO_3/mont K10 in good yields. This method is simple, requires cheaper reagents, the products are easy to separate from reaction mixture, and the catalyst(s) is reusable at least three times with negligible loss of activity. These catalysts can be used for many acid catalyzed organic transformations wherein mild acidity is required and investigations are under progress.

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