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Mechanochemical assisted acetylation of aromatic amines, phenols and thiol catalysed by RHA-SiO_2 (NPs)@BO_3H_3

Raju Shekhanavar, Santosh Khatavi & Kantharaju Kamanna*
Peptide and Medicinal Chemistry Research Laboratory, Department of Chemistry, Rani Channamma University,
P-B, NH-4, Belagavi 591 156, India
*E-mail: kk@rcub.ac.in

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In this work, rice husk-derived silica nanoparticles (RHA-SiO_2-NPs) are synthesized and further surface functionalized with boric acid to avoid tedious recycling of the silica NPs and also increasing Lewis acid strength of the silica. The prepared heterogeneous catalysts (RHA-SiO_2NPs@BO_3H_3) demonstrated application in the formation of acetyl derivatives of aryl amine, thiol and phenol in the presence of acetic anhydride under grindstone method gave excellent product isolation (98% yield in 5-8 min). The benefit of this method found simple, efficient, solvent-free and reusable. The catalyst prepared in this work derived from the agro-waste and functionalized for the efficient catalytic activity.

Keywords: Aromatic amine, Grindstone, Mechanochemical acetylation, Phenol, Recyclable, Rice husk

Introduction

Present days organic chemists are developing greener, solvent-free, and recyclable heterogeneous catalysts as an alternative to conventional methods in the fine chemicals and pharmaceutical industries[1-7]. Silica displays many advantageous properties such as excellent chemical and thermal stability[8,9], high surface area[10-12], good accessibility, and surface modification making it easier to provide efficient catalytic materials[13]. In silica nanoparticles, the terminal silanol hydrogen has a positive charge, and the density of the hydroxyl is very small, so it can be considered as an Bronsted acid[14,15]. The larger hydroxyl polarization is achieved by coating a silica surface with a strong Bronsted acid such as Boric acid[16]. The coated Boric acid generates a positive charge with a comparatively stronger acidic nature than the silanol group. They exist in well-prepared amorphous long-range structured silica borate[17-20]. Inspired by the vast catalytic applications of silica-based materials[21,22], the extensive use of silica and its composites is used in the chemical industries[23,24]. To meet the required demand, researchers explored alternative sources of silica from the nature[25-27].

Rice husk is an agro-waste material with 90–94% silica present, and abundant in all rice-producing countries with an annual production of about 80 million tons[28,29]. The application of the rice husk is poorly explored, in fuel extraction is used in small portions, but the majority of the amount burned leads to the emission of smoke, which causes human health and global climate[30-33]. Hence, its diverse utilization greatly indeed to prepare silicon and it's composite as a potential heterogeneous catalyst for the diversified applications for fine chemical industries and pharmaceuticals[34-36].

The pharmaceutical and fine chemical industries extensively use the oxidative transformation of amines, phenols, and thiols through the catalytic pathway[37]. The transformation can be achieved both using basic and acidic conditions, but heterogeneous catalysts with Lewis acid properties reported efficient transformation of the acetylation of amines, phenols, and thiols. Some of the catalysts reported in the literature are basic Al_2O_3[38], Fe_2O_3[39], $HClO_4/SiO_2$[40], Silica-H_2SO_4@Fe_3O_4[41], Amberlyst-15[42], nano-Nickel aluminates[43], Citric acid@Fe_3O_4[44], $Fe(OTf)_3$[45], $Al(HSO_4)_3$[46], $ZnCl_2$[47], P_4VP-HX [Poly(4-vinylpyridine)][48] ethyl acetate/AcOH[49], $MgBr_2$[50], Iodine[51], Zinc dust[52], SiO_2-$M(acac)_n$[53], Heteropoly acid catalyst ($H_6P_2W_{18}O_{62}\cdot 24.H_2O$)[54], Zeolite H-FER[55], silver-graphene oxide nano-composite[56], $Bi(OTf)_3$[57], and more have been applied for the acetylation to aromatic amines, phenols and thiols derivatives. Using these catalysts, we noticed certain disadvantages of organic synthesis, like toxicity of the reagent or solvent used, and harsh reaction conditions[58-60]. In addition to this, solvent-free synthesis, and recyclable catalysts have valuable environment and economical production plans for range of organic transformations[61]. Herein, we explored modified agro-waste-derived silica nanoparticles as a heterogeneous catalyst for an efficient, simple, greener, solvent-free, inexpensive, and reusable catalyst for the acetylation of aromatic amines, thiols, and phenols using acetic anhydride under simple grinding method.

Experimental Section

Reagents used in this work were purchased from SD-fine and AVRA chemicals and directly used as it received. The melting points were determined by the open capillary method and are uncorrected. The RHA and catalyst XRD data were collected on a Rigaku Japan tabletop instrument. The Reverse Phase High performance Liquid Chromatography (RP-HPLC) was performed in Shimadzu with a C_{18} analytical column with mobile phase ACN-H_2O was used. FT-IR spectra were collected in Thermo Fischer scientific using KBr pellet method, and ^{1}H- and ^{13}C-NMR spectra were collected in an Agilent spectrometer at 400 MHz in $CDCl_3$ solvent. The chemical shifts are reported in ppm (δ) relative to tetramethyl-silane as an internal standard, and mass spectra were obtained by Waters Synapt G2, USA.

Preparation of rice husk-SiO$_2$ ash

Rice husk collected from the local rice milling, washed two times with distilled water to remove dirt and muddy impurities, and then dried in sunlight shadow for two days. Then burnt husk at 700°C for 6 h in a muffle furnace gave white ash, ground to fine powder (RHA), and characterized by ^{29} Si-NMR and XRD[17].

Preparation of rice husk-SiO$_2$ nanoparticles

RHA-SiO$_2$ (2.5 g) was dispersed in 250 mL of a 0.5 M aqueous NaOH solution and heated at 100°C for 4 h under stirring to dissolve silica and produce sodium silicate. The solution was filtered to remove unreacted impurities, and then a transparent filtrate of sodium silicate solution was allowed to cool at room temperature and titrated with 10% H_2SO_4 to pH 7 under stirring. The sodium silicate present is to be neutralized with diluted sulfuric acid to precipitate silica. The solution continued stirring for 24 h, and was then aged slowly for the precipitation. The obtained gel was fragmented, filtered, and washed with water to remove the sulphate salt. The clean silica nanoparticles (SNPs) was dried overnight under vacuum to remove water and stored in vacuum desicators[17]. Further, the XRD and SEM images were collected for the SNPs and given in the supporting material (Fig. S1).

Preparation of rice-husk SNPs supported-boric acid catalyst [RHA-SiO$_2$(NPs) @BO$_3$H$_3$]

1.0 g Boric acid with 20 mL distilled water was taken in a 100 mL round bottom flask and heated to 60-80°C for a few minutes. To this powdered rice husk-SiO$_2$ nanoparticles were added gradually with constant stirring, refluxed up to 5 h, and water was removed under vacuum, then the residue was dried at 100°C for 6-7 h under vacuum gave free flow white powder [17]. Further the sample was characterized by XRD and SEM-EDX data provided in supporting information (Fig. S2).

General procedure for the acetylation of aromatic amines, thiophenol, and phenols

In a clean and dry mortar, aromatic amine, phenol, or thiol (1 mmol), catalyst (160 mg), and acetic anhydride (1.2 mL) were added to the mortar and ground till completion of the reaction. The reaction completion is monitored by TLC. After the reaction, the product was extracted using ethyl acetate. The resulting organic layer was thoroughly washed with water, dried over Na_2SO_4 and evaporated solvent and obtained residue was precipitated by adding petroleum ether gave pure product isolation. The obtained product was characterized by FT-IR, ^{1}H- and ^{13}C-NMR, and HR-MS (ESI). Further, the used catalyst was recycled by washing with ethanol, dried in a hot air oven at 80°C for 4 h, and reused.

Selected spectral data

Acetanilide ***(3a):*** White powder; FT-IR(KBr); ν 3290 (NH), 3030 (CH), 1663,1620, cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-*d*$_6$); δ 7.26 (s, NH), 6.54 (m, 5H), 3.32 (s, 3H); ^{13}C-NMR (400 MHz; DMSO-*d*$_6$) δ 168.81, 166.93, 143.33, 130.13, 124.38, 18.51 and 24.21 ppm; Anal. (Calcd.) For C_8H_9ON; C, 71.08; H, 6.71; N, 10.36; (Found): C, 71.01; H, 6.60; N, 10.23.

N-Acylanisidine ***(3d):*** White powder; FT-IR(KBr); ν 3243 (NH), 1647, 1606, 1560 cm^{-1}; ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.38 (d, 3H, *J* = 9.16 Hz), 6.84 (d, 2H, *J* = 9.16 Hz), 3.78 (s, 3H), 2.14 (s, 3H); ^{13}C-NMR (100 MHz; DMSO-*d*$_6$) δ 168.30, 156.23, 130.19, 121.49, 114.01, 55.48 and 24.12 ppm; Anal. (Calcd.) $C_9NO_2H_{11}$; C, 65.44; H, 6.71; N, 8.48; O, 19.37, (Found): C, 65.64; H, 6.93; N, 8.70; O, 19.20.

N-(4-Nitrophenyl) acetamide ***(3e):*** Yellowish solid; RT-IR (KBr); ν 3481 (NH), 3362, 3222 (NH), 1676, 1631, 1595 cm^{-1}; ^{1}H-NMR (400 MHz; $CDCl_3$) δ 10.56 (br, s, 1H), 8.21(d, 2H, *J* = 8 Hz), 7.82 (d, 2H, *J* = 8 Hz), 2.08 (s, 3H); ^{13}C-NMR (400 MHz; $CDCl_3$) δ 169.45, 145.55, 142.20, 125.40, 118.15 and 24.43 ppm; Anal. (Calcd.) $C_8N_2O_3H_8$; C, 53.33; H, 4.48; N, 15.55; O, 27.64, (Found): C, 53.22; H, 4.59; N, 15.33; O, 26.86.

N-(4-Hydroxyphenyl) acetanilide ***(3g):*** White powder; FT-IR(KBr); ν 3326 (NH), 3161 (CH), 1655, 1610, 1565, cm^{-1}; ^{1}H-NMR (400 MHz; DMSO-*d*$_6$) δ 9.64 (br, s, 1H), 9.13 (s, 1H), 7.33 (d, 2H, *J* = 8.7 Hz), 6.66 (d, 2H, *J* = 8.7 Hz) 1.97 (s, 3H); ^{13}C-NMR (400 MHz; DMSO-*d*$_6$) δ 167.50, 153.12, 131.00, 120.08, 115.26 and 23.57 ppm; Anal. (Calcd.) $C_8NO_2H_9$; C, 63.56; H, 6.00; N, 9.27; O, 21.17, (Found): C, 63.16; H, 6.50; N, 9.17; O, 21.27.

4-Acetamidobenzoic acid ***(3f):*** White powder; FT-IR (KBr); ν 3305 (NH), 2924 (CH), 1671, 1522; ^{1}H-NMR (400 MHz; DMSO-*d*$_6$) δ 12.66 (br, s, 1H), 10.23 (br, 1H), 7.87 (d, 2H, *J* = 8.7 Hz), 7.68 (d, 2H, *J* = 8.7 Hz), 2.07 (s, 3H); ^{13}C-NMR (400 MHz; DMSO-*d*$_6$) δ 168.80, 166.91, 143.23, 130.33, 124.28, 18.16 and 24.81 ppm; Anal. (Calcd.) $C_9NO_3H_9$; C, 60.33; H, 5.06; N, 7.82; O, 26.79; (Found): C, 60.00; H, 5.39; N, 7.60; O, 27.09

N-(2-methoxyphenyl)acetamide ***(3h):*** Light brown; FT-IR (KBr); ν 3305 (NH), 2924 (CH), 1671, 1522; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 7.9 Hz, 1H), 7.01 (td, *J* = 7.9 Hz, 1H), 6.98 – 6.89 (m, *J* = 7.7, 6.7 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 3.86 (s, 3H), 2.18 (s, 3H). ^{13}C-NMR (400 MHz; $CDCl_3$) δ 23.01, 54.84, 112.83, 120.32, 121.23, 126.90, 128.22, 149.60 and 168.90 ppm; Anal. (Calcd.) $C_9H_{11}NO_2$; C, 65.44; H, 6.71; N, 8.48; O, 19.37, (Found): C, 65.42; H, 6.69; N, 8.45; O, 19.35 [18]

N-(1-Phenylethyl)acetamide ***(3l):*** White powder; FT-IR (KBr); ν 3292 (NH), 3063 (CH), 1719, 1539 cm^{-1}; ^{1}H-NMR (400 MHz; DMSO-*d*$_6$) δ 8.36 (Br, 1H), 7.33 (Br, s, 1H), 7.31 (d, 2H, *J* = 7.7 Hz), 7.25 (d, 2H, *J* = 7.7 Hz), 7.21 (s, 1H), 2.07 (s, 3H), 1.87 (s, 3H); ^{13}C-NMR (400 MHz; DMSO-*d*$_6$) δ 169.77, 140.00, 128.73, 127.70, 127.20, 42.56, 40.50, 39.46, 39.25, 22.99 ppm; Anal. (Calcd.) $C_{10}H_{13}NO$; C, 60.33; H, 5.06; N, 7.82; O, 26.79, (Found): C, 60.00; H, 5.39; N, 7.60; O, 27.09.

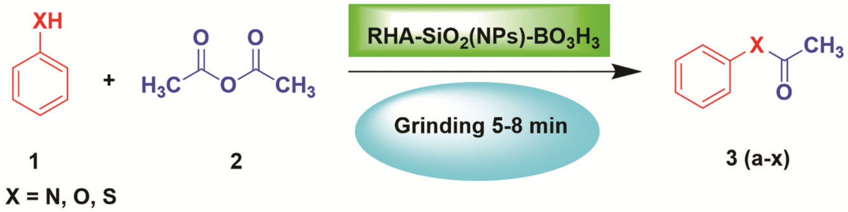
Phenyl acetate ***(3r):*** White powder; FT-IR (KBr); ν 3060 (CH), 2926 (CH), 1745, 1595 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$); δ 7.05 (s, 5H), 7.23 (m, 4H), 4.70 (s, 2H), 2.12 (s, 3H); ^{13}C-NMR (400 MHz; DMSO-*d*$_6$); δ 168.82, 166.93, 143.32, 130.34, 124.85, 18.16 and 24.17 ppm; Anal. (Calcd.) for $C_9H_9O_4N$; C 55.38, H, 4.64; N 7.17, (Found); C, 55.38; H, 4.61, N 7.15.

2-Naphthylacetate ***(3v):*** White powder; FT-IR (KBr); ν 2926 (CH), 1745, 1600 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$); δ 7.05 (m, 7H); 2.12 (s, 3H); ^{13}C-NMR (400 MHz; DMSO-*d*$_6$); δ168.80, 166.91, 143.34, 130.37, 124.88, 18.13 and 24.14 ppm; Anal. (Calcd.) $C_{12}H_{10}O_2$; C, 77.40; H, 5.41; H, 5.39, (Found): C, 77.60; H, 5.21; H, 5.39.

Results and Discussion

The previously reported procedure for the isolation of silica from RHA is extended to RHA-SiO_2 nanoparticle preparation and surface functionalization by BO_3H_3[17]. The powdered XRD pattern revealed both RHA-SiO_2(NPs) (Fig. S1a) and RHA-SiO_2(NPs)-BO_3H_3 (Fig. S1b) peaks at 26° for amorphous SiO_2 NPs, and sharp intense peak at 28° observed due to the presence of the Boron. Hence, by comparing both XRD patterns (Figs S1a & 1b), it was revealed that BO_3H_3 functionalized on RHA-SiO_2 NPs surface, and also collected SEM images of these two silica materials to see the surface morphology (Figs S2 & S3). To check the catalytic activity of the prepared RHA-silica-coated boric acid, we explored its application in the acetylation of aromatic amines, thiols, and phenol substrates under solvent-free condition by grinding method (Scheme 1). The minimal dose of catalyst loading required for the 1 mmol of the reaction is investigated in a model reaction of aniline (1 mmol) and acetic anhydride (1.2 mmol) in the presence of a 20 mg of the catalyst variation at room temperature (Table 1, entries 1–10). The comparative variation of the catalyst and resulted product isolation as a percentage of yields in a model reaction is presented in Table 1.

Further the reaction was performed in the absence of catalyst (entry 1, Table 1) showed no product formation even after 10 min of grinding (monitored by TLC). The preference for acetanilide product isolation gradually increased with an increase in the amount of catalyst (20 to 160 mg) in a model reaction, this might be a sufficient catalyst surface available for catalysis. However, at 160 mg, the catalyst dose in a model reaction gave excellent yields of the product acetanilide in just 4 min at room temperature (Table 1, entry 8). Further increased catalyst loading (180 mg and 200 mg) in a model reaction did not



Scheme 1 — General acetylation reaction of amine, thiol, and phenol

Table 1 — Optimization of the catalyst required for the 1 mmol scale reaction

Entry	Catalyst	Amount of catalyst (mg)	Yield (%)
1	RHA-SiO_2(NPs)-BO_3H_3	-	ND*
2		40	Nil
3		60	Nil
4		80	36
5		100	58
6		120	72
7		140	92
8		160	98
9		180	98
10		200	98

* ND = Product isolation not detected

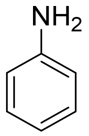
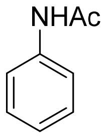
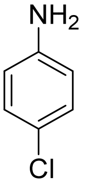
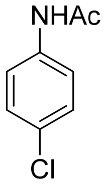
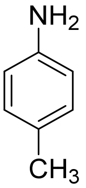
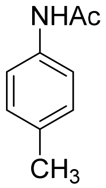
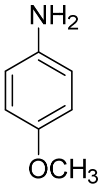
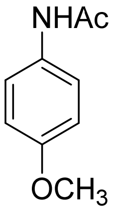
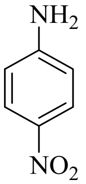
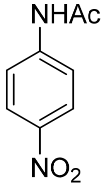
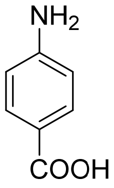
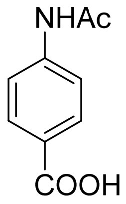
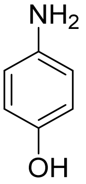
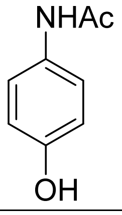
result in any incremental increase in the product isolation (Table 1, entries 9–10). Additionally, we also carried out a model reaction at an optimized catalyst dose of 160 mg in the presence of organic solvents, *viz.*, ethyl acetate, toluene, acetone, $CHCl_3$, and acetonitrile. However, the product isolation in these solvent systems was poor compared to the reaction carried out in mechanochemical. Therefore, in the present work solvent-free condition is chosen for the acetylation of aryl amines.

To explain wide scope of this method for acetylation, we extended to acetylation of alkyl amines, alcohols, thiols, and phenols. The acetylation of aliphatic amines and alcohol substrates showed poor reaction progress in the presence of acetic anhydride. In these functional groups, the acetylation reaction attempted did not show any product formation (TLC monitored). The extended acetylation of phenol and aromatic thiols under similar optimized reaction conditions gave acetylated products in 85–95% product isolation with little grinding time as compared to aromatic amines (Table 2). The acetylation of various aliphatic and aromatic substituted amines was attempted using solvent-free conditions with an optimized catalyst. Surprisingly, aromatic primary amines are efficiently acetylated compared to aliphatic amines (Table 2, entries 1-25). The selected acetyl derivatives spectral data of FT-IR, ^{1}H-, ^{13}C-NMR and HR-MS are available in supporting information (Figs S5-S14).

The catalyst efficiently acetylated aromatic amines, phenols, and aromatic thiols at room temperature grinding method. To study the elution time of aniline acetylated product acetanilide, the product dissolved in acetonitrile and filtered, and clear solution is injected into RP-HPLC on a Shimadzu C_{18} analytical column in a binary gradient system of acetonitrile-water system solvent with a flow rate of 1 mL/min. The aniline was eluted at 80% acetonitrile and water, and the acetanilide was eluted at 84% acetonitrile and water, with R_t values of 12.5 and 8.75 min, respectively (Fig. 1). The same protocol was repeated for another 2-aminophenol and its acetylated product: 2-aminophenol eluted at 81% ACN-H_2O (Fig. 2a), acetylated 2-aminophenol (1 mmol acetic anhydride) eluted at 83% ACN-H_2O (Fig. 2b), and acetylated 2-aminophenol (2 mmol acetic anhydride) eluted at 85% ACN-H_2O (Fig. 2c) system with R_t values of 7.50, 7.75, and 7.84 min, respectively.

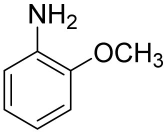
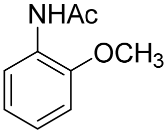
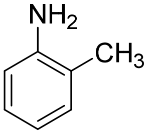
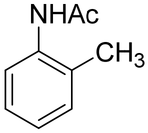
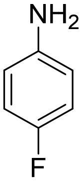
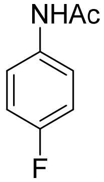
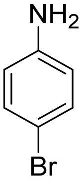
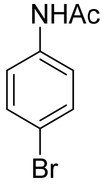
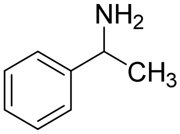
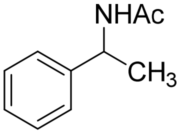
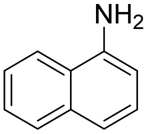
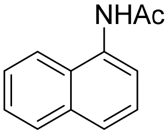
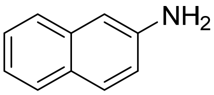
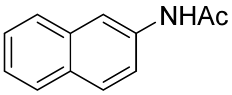
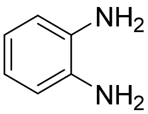
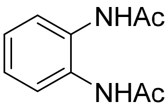
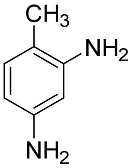
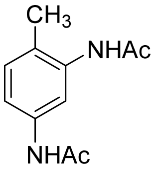
Furthermore, we studied the comparative methods reported in the literature for acetylation of aryl amines, including percentage yield, catalyst type, reaction time, and solvent used by previously reported methods tabulated in Table 3 (entries 1–14). Reactions in the presence of AcOH, LiCl, and ATPB are carried out and take longer reaction times (entries 2, 4, and 9, Table 3), and some of the catalysts are hazardous to the environment (entries 5-8, Table 3) and unpredictable (entries 10–12 and 14, Table 3).

Table 2 — Acetylation of aromatic amines, phenols and thiols

Entry	Reactant	Product	m.p (°C)	Yield%
1		 3a	113-114	98
2		 3b	167-169	89
3		 3c	148-150	91
4		 3d	128-130	93
5		 3e	145-147	78
6		 3f	319-321	79
7			168-171	92

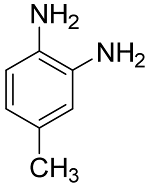
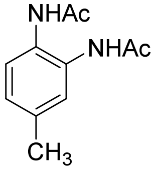
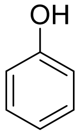
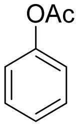
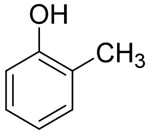
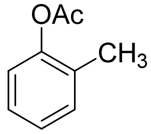
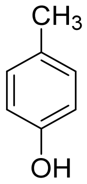
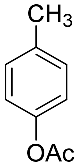
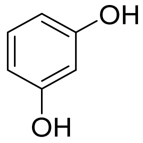
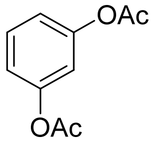
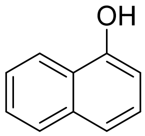
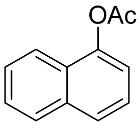
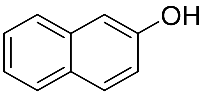
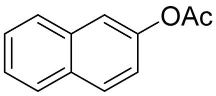
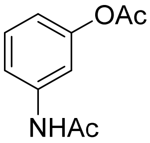
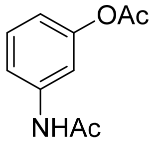
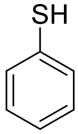
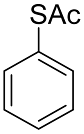
(*Contd.*)

Table 2 — Acetylation of aromatic amines, phenols and thiols

Entry	Reactant	Product	m.p (°C)	Yield%
8		 3h	84-86	78
9		 3i	-	85
10		 3j	146-148	81
11		 3k	165-167	83
12		 3l	189-191	88
13		 3m	344-346	81
14		 3n	243-245	79
15		 3o	214-216	83
16		 3p	198-200	87

(*Contd.*)

Table 2 — Acetylation of aromatic amines, phenols and thiols

Entry	Reactant	Product	m.p (°C)	Yield%
17		 3q	188-190	84
18		 3r	192-194	97
19		 3s	152-154	91
20		 3t	148-150	86
21		 3u	-	87
22		 3v	44-46	86
23		 3w	68-70	84
24		 3x	119-121	67
25		 3y	98-100	77

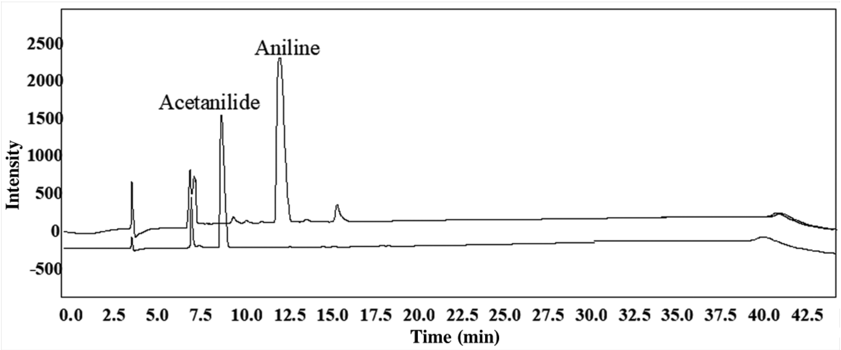


Fig. 1 — RP-HPLC profile of acetanilide and aniline

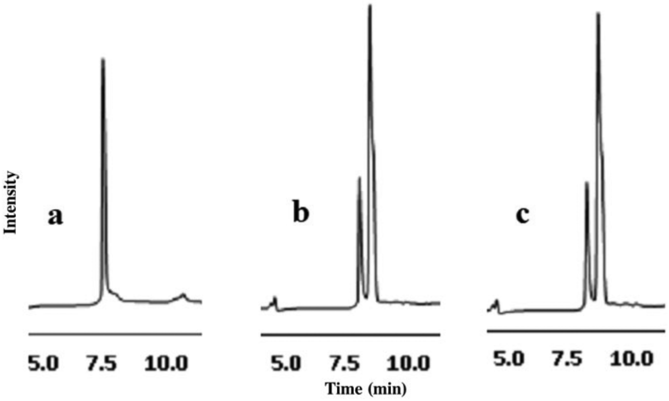


Fig. 2 — RP-HPLC profile of acetylated 2-aminophenol eluted at (a) 81%, (b) 83% and (c) 85% ACN-H_2O

Table 3 — Comparison of the different catalysts reported for acetylation of aryl amine with the present method.

Entry	Catalyst	Time	Yield (%)	Ref.
1	Aq. Extract of pods acacia conicinna10%, 10 mL	30-60 min	96	62
2	AcOH (10 mol%), 80 °C	20 h	87	60
3	Acetyl chloride/K_2CO_3, PTC solvent, r.t^a	15-20 min	89	63
4	LiCl	3-5 h	95	64
5	Al_2O_3, Acetic anhydride	40 min	98	65
6	Al(Cat.)/CH_3CN, Sonication	1- 4 min	97	66
7	$(CH_3CO)_2O$/Amberlyst-15, r.t	30-120 min	96	42
8	Anhy. $NiCl_2$ (0.20 mol %)	80 min	98	67
9	Acetonyltriphenylphosphoniumbromide (ATPB)	25 min-1.5h h	93	68
10	Fe_3O_4@Citricacid (10 mg), 45 °C	45 min	95	44
11	$MgCl_2.5H_2O$ (0.20 mol%), r.t	30-70 min	96	69
12	$CoCl_2$ (1 mol %) AcCl (1.2 eqt.)	20-30 min	99	70
13	Copper perchlorate (0.05 mol%), Ac_2O	1-15 min	97	71
14	HPA (0.01g), Ac_2O, r.t	10-75 min	98	54
15	RHA-SiO_2(NPs)-BO_3H_3, Mechanochemical	5-8 min	98	Present method

The experimental results revealed that, the present investigated catalyst has several added advantages including being greener (entry 15, Table 3). Overall, the present catalysts showed an inexpensive, simple reaction set-up and solvent-free condition, giving excellent product isolation with reuse of the catalysts up to four cycles of the reaction.

Moreover, we also examined the reusability of the first cycle used catalysts for the acetylation of aniline under an optimized dose catalyst (Fig. S4). In each reaction cycle, the catalyst is separated, washed two times with deionized water, followed by one-time ethanol, dried overnight at 100 °C, and reused for the next cycle of the reaction. The recycled series of reaction isolated yield in a model reaction is presented in Fig. S4, and showed not much change in the catalytic activity up to the fourth cycle of the reaction, but in the fifth cycle of the reaction, there was a sudden drop in the isolation of the product by 10% less. Moreover, to investigate the exact mechanistic pathway for the acetylation reaction by the catalyst, it was not clear, but probably the carbonyl group of the acetic anhydride closure towards the surface of the catalyst. This inference suggests that, the nucleophilic nature of N, O, and S atom attack to the more electrophilic carbonyl sites resulting unstable intermediates that lead to the formation of stable acetate.

Conclusion

Agro-waste derived silica-coated boric acid (RHA-SiO_2(NPs)-BO_3H_3) as a Lewis acid demonstrated application for the oxidative transformation of aryl amines, phenols, and thiols to acetylation using acetic anhydride under solvent-free grinding methods. The present protocol has many advantages such as simple, solvent-free, reusable catalyst up to fourth cycle, and inexpensive gave excellent product isolation in 5-8 min (98% yields). Further selected product was characterized by various spectral analyses, and showed pure products isolation. The reaction optimization was performed in RP-HPLC, and showed clear consumption of the reactants to lead the product in 4 min. Additionally, the catalysts were recycled up to 4 times without any accountable loss in its catalytic activity.

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Supplementary Information

Supplementary information is available on the website http://nopr.niscpr.res.in/handle/123456789.

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