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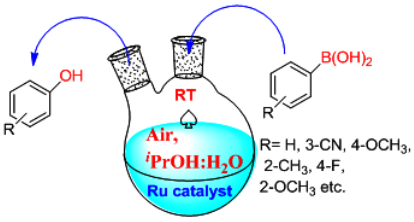

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# Grafting of Ru(III) complex onto nanosilica and its implication as heterogeneous catalyst for aerobic oxidative hydroxylation of arylboronic acids

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ABSTRACT

**Abstract:** An ecofriendly and highly efficient protocol for aerobic oxidative hydroxylation of aryl and heteroaryl boronic acids catalyzed by Ru(III) imine complex immobilized on nanosilica, derived from rice husk, has been developed. The main significance of this protocol is the base free and aerobic reaction condition at room temperature, short reaction time, aqueous reaction medium and excellent yield of the product. This heterogeneous catalyst is reusable up to sixth cycle without loss in activity.
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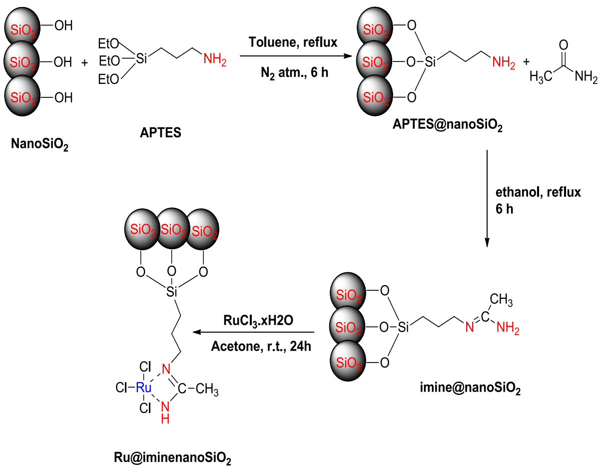
## 1. Introduction

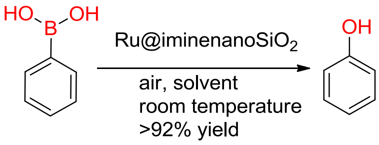
Phenols and their derivatives occurs widely in various natural products, pharmaceuticals, agrochemicals; they also serve as building block of many biologically and synthetically important compounds[1] besides acting as antioxidant, antimicrobial, anti-inflammatory, anticancer and anti-allergenic agents[2].Among the various synthetic protocols for the synthesis of phenols, nucleophilic aromatic substitution of aryl halides and Pd catalysed conversion of aryl halides, copper-catalyzed transformation of diazo arene and benzene are well known[3]. However, the harsh reaction conditions, high cost involved in Pd catalyzed protocols as well as difficulty involved to control the diazotisation of the amino groups to aryl diazonium ions make these methods less attractive.[4] In recent years, the synthetic route for phenols and other functional groups like aryl halides, aryl amines, aryl sulphones using arylboronic acid and its derivatives have emerged as important ones. The conversion of aryl boronic acids to phenols in these protocols mainly involves the use $CuSO_4$–phenanthrolin[5], $I_2$–$H_2O_2$,[6], alumina-$H_2O_2$[7], $NH_2OH$,[8] potassium peroxy monosulfate,[9] $H_3BO_3$–$H_2O_2$,[10] $NaClO_2$,[11] supported silver nano particle–$H_2O_2$, [12] Biosilica –$H_2O_2$[13] etc

Although some of the above mentioned methodologies often show excellent results, in the majority of cases an additional oxidant is required to maximize the yield of the product. Furthermore, the use of harmful toxic organic solvents, ligands/bases, long reaction time makes these processes less attractive.[14] However, it is observed from the reported results that the most of such reactions are carried out in presence of $H_2O_2$ as source of oxygen and KOH[8,15] as the base, while the protocols involving air as sole oxidant is scanty.[16] Since molecular oxygen is considered as a highly environment friendly oxidant in modern organic synthesis, the efforts have been made for the development of protocols for synthesis of phenols taking arylboronic acid as precursor. In heterogeneous catalysis, the catalysts involving metals like Pd, Ru, Cu etc. immobilized on silica is an important area of recent research. The use of nanosilica derived from rice husk makes them eco-compatible. Alternatively, use of silica for the purpose of immobilization of metals, obtained from rice husk, an agro waste product is much greener due to its cost effectiveness, environment friendly route, easy preparation process and easy availability [17,18]Therefore, considering the above, we have developed a new methodology for the synthesis of phenols under aerobic condition involving no base, ligand and additives at room temperature within short reaction time. The nanosilica immobilized Ru(III) Schiff base heterogeneous catalyst was found to be efficient and can be reused up to sixth cycle without losing effectiveness.



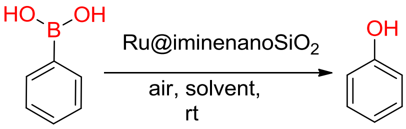
Scheme 1: Preparation of nanosilica immobilized Ru(III) Schif base complex

After synthesizing the nanosilica and nanosilica based catalyst (as shown in Scheme 1) by using methods reported earlier[19], our next step is to investigate its catalytic efficiency in synthesis of phenol.[20] The molecular oxygen present in air has been widely used as a green oxidant in synthesis.[21] Thus we have observed that phenylboronic acid undergoes oxidative transformation to the phenol in the presence of Ru@imine-nanoSiO$_2$ in excellent yields under aerobic condition (Scheme 2). This positive result encouraged us to perform a series of control experiment. No conversion was observed in the absence of any one of these reaction component (Table 1, entries 1–3 vs 4). These results show that the solvent, Ru@imine-nanoSiO$_2$ and air are all essential for this reaction, indicating their key roles in this transformation reaction.



Scheme 2: Synthesis of phenol by Ru@iminenanoSiO$_2$ catalyst

**Table 1:** Screening and control experiment [a]

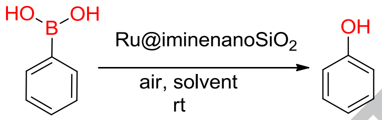


| **Entry** | **Air** | **Solvent** | **Catalyst** | **Yield (%)** |
|---|---|---|---|---|
| 1 | - | + | + | Trace |
| 2 | + | - | + | NR |
| 3 | + | + | - | NR |
| 4 | + | + | + | 92 |

[a] Reaction condition: phenyl boronic acid (1mmol), catalyst (5 mg), solvent (3 ml); reaction time 60 min; NR- no reaction

Next, we optimized the reaction conditions taking phenyl boronic acid as model substrate and 5 mg of Ru@imine-nanoSiO$_2$ catalyst. A survey of solvents showed that the transformation was preceded in both protic and aprotic solvents although the reaction was not very sensitive to the reaction media. DMSO, DMF, CH$_3$CN, MeOH, and $^i$PrOH were all compatible and give good to excellent yield of product (Table 2, entries 1–8). Among them $^i$PrOH was found to be the most efficient solvent providing highest yields within a very short reaction time, whereas with H$_2$O the yield decreased to 65% (Table 2, entry 6). When we mixed H$_2$O and $^i$PrOH in 1:1 proportion and used as solvent, its yield was considerably increased. In order to optimize the amount of catalyst a series of catalytic test were done with phenyl boronic acid (Table 2, entries 9-12). We interestingly noticed that the increase in quantity of Ru catalyst did not improve the product yield whereas a decrease in quantity lowered the yield (Table2, entries11–12). Again, imine@NanoSiO$_2$ and NanoSiO$_2$ does not itself catalyze the reaction (Table 2, entries 9-10). When the reaction was carried out using H$_2$O$_2$ as an oxidant no significant conversion of the yield was achieved. (Table 2, entry 13). Based on the observation of entries 7, 11, and 12, it was evident that a combination of 5 mg of Ru catalyst and $^i$PrOH:H$_2$O as solvent was necessary for the quick and effective conversion of phenyl boronic acid to phenol.

**Table 2:** Optimization of reaction condition

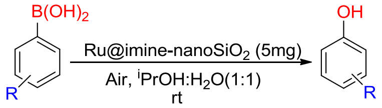


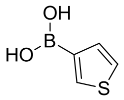
| Entry | Solvent | Catalyst | Time (min) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | DMSO | Ru@iminenanoSiO$_2$ | 60 | 78 |
| 2 | DMF | Ru@iminenanoSiO$_2$ | 50 | 82 |
| 3 | MeOH | Ru@iminenanoSiO$_2$ | 45 | 82 |
| 4 | CH$_3$CN | Ru@iminenanoSiO$_2$ | 45 | 80 |
| 5 | $^i$PrOH | Ru@iminenanoSiO$_2$ | 45 | 89 |
| 6 | H$_2$O | Ru@iminenanoSiO$_2$ | 80 | 65 |
| 7 | $^i$PrOH: H$_2$O (1:1) | Ru@iminenanoSiO$_2$ | 45 | 92 |
| 8 | DMF: H$_2$O(1:1) | Ru@iminenanoSiO$_2$ | 60 | 80 |
| 9 | $^i$PrOH: H$_2$O (1:1) | Imine@nanoSiO$_2$ | 60 | Trace |
| 10 | $^i$PrOH: H$_2$O (1:1) | NanoSiO$_2$ | 60 | Trace |
| 11 | $^i$PrOH: H$_2$O (1:1) | Ru@iminenanoSiO$_2$ | 45 | 92[b] |
| 12 | $^i$PrOH: H$_2$O (1:1) | Ru@iminenanoSiO$_2$ | 50 | 88[c] |
| 13 | $^i$PrOH: H$_2$O (1:1) | Ru@iminenanoSiO$_2$ | 40 | 92[d] |

[a] isolated yield, [b] amount of Ru catalyst used 10 mg, [c] amount of catalyst used 3 mg,[d] H$_2$O$_2$ used as oxidant

To understand the versatility of our current methodology with Ru@imine-nanoSiO$_2$ as catalyst, we have tried to extend the scope with a wide range of diverse arylboronic acids under optimized reaction conditions (Table 3). In general, aryl boronic acids with either electron-withdrawing or electron-donating substituents such as Cl, F, OMe, CN, Me, C(CH$_3$)$_3$ (Table 3, entries 2–10) provided excellent yields in this transformation reaction (87–95%). The current protocol also well-suited with heteroaryl boronic acid, but comparatively long reaction time was needed (Table 3, entry 11).

**Table 3**: Ru catalysed organic synthesis of phenol[a]



| **Entry** | **Substrate (R)** | **Time (min)** | **Yield(%)[b]** |
|---|---|---|---|
| 1 | H | 45 | 92 |
| 2 | 3-CH$_3$ | 50 | 89 |
| 3 | 4-Cl | 65 | 92 |
| 4 | 2-CH$_3$ | 50 | 90 |
| 5 | 3-CN | 48 | 89 |
| 6 | 2-CH$_3$O | 50 | 95 |
| 7 | 4-CH$_3$ | 55 | 87 |
| 8 | 4-C(CH$_3$)$_3$ | 50 | 90 |
| 9 | 4-F | 65 | 90 |
| 10 | 4-CH$_3$O | 60 | 90 |
| 11 |  | 110 | 87 |

[a] Reaction condition: phenyl boronic acid (1mmol), catalyst (5 mg), solvent (4 ml), rt: 30 °C, [b] isolated yield

From a green chemistry viewpoint, the reusability of catalysts[22] makes them more attractive and one of advantages of using heterogeneous catalyst. Therefore the reusability of the Ru catalyst was performed. Based on our reusability test we found that the Ru@imine–nano$SiO_2$ catalyst could be consistently used up to six consecutive reactions of phenylboronic acid to give phenol (Fig. 1). After completion of the first cycle, it could be easily recovered by centrifugation, and thoroughly washing with $^i$PrOH:$H_2O$ followed by EtOAc and drying inoven, it can be used again for fresh reaction. The Ru content after 6th run was determined by ICP-AES analysis, and found to be below detection level. Amazingly, the catalyst remained efficient and gives successful conversion to phenol with excellent yields up to the sixth run[12]

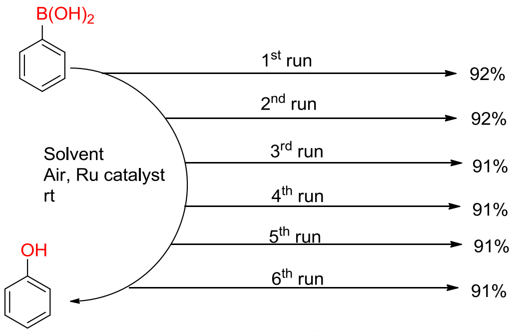


**Fig.1: Reusability of catalyst**

In summary, we have developed a clean and effeicient protocol for the organic transformation of arylboronic acids to phenols using bio-sourced nanosilica derived Ru@imine-nano$SiO_2$ as heterogeneous catalyst. The advantageous features of this protocol include (a) use of air as green oxidant in place other oxidants; (b) it is a base and ligand free system; (c) take place within short reaction time and at room temperature (d) use of water as co-solvent (e) the current protocol is also effective with a various substituted aryl and heteroaryl boronic acids giving phenols as products in good to excellent yields.

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20. General procedure for the hydroxylation of arylboronic acid: A 50 mL round bottom flask was charged with arylboronic acid (1 mmol), 5 mg Ru catalyst and 4 ml $^i$PrOH: $H_2O$ (1:1). The reaction mixture was stirred at room temperature under aerobic condition. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with 20 mL of water and extracted with diethyl ether. The combined organic layers were washed with brine and dried over by anhydrous $Na_2SO_4$ and evaporated in a rotary evaporator under reduced pressure. The crude was purified by column chromatography on silica gel (hexane:ethyl acetate, 9:1) to afford the desired product. The purity of the compound was confirmed by $^1$H NMR, $^{13}$C NMR.
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22. General procedure for reusability test: After completeion of the reaction, the catalyst was isolated from the reaction mixture by simple centrifugation process and washed with ethyl acetate and water to remove the organic contaminants. After getting the solid part of catalyst, it was drying at 110 °C in an oven for whole night. Then catalyst was used for further fresh reaction taking phenylboronic acid as substrate. Reaction conditions were kept similar to the other reactions.

**Highlight:**

- ✓ Heterogeneous Ru(III) catalyst for oxidative hydroxylation of arylboronic acids
- ✓ Air is used as oxidant
- ✓ The catalyst is reusable up to sixth cycle without any loss in activity.