A heterogeneous iron-catalyzed (8wt%Fe/SBA-15) mediated direct alkylation of benzyl alcohol with aryl boronic acid in the absence of base and additive via C-O bond activation is demonstrated. This catalyst system led to an efficient Friedel-crafts alkylation reaction. The acidic site in the catalyst system had been confirmed by NH$_3$-TPD, which shows the presence of three different acidic sites viz., weak, moderated, and strong acid sites. The catalyst showed five times recyclable ability.

Carbon-carbon coupling reaction using transition metal catalyst plays a significant role in organic chemistry\cite{1}. The C–O bond activation engaging with 4d and 5d transition metals have been identified as an exciting tool for the functionalization and assembly of interesting organic molecules, owing to their use in biochemistry, material sciences, and pharmaceutical industries\cite{2}. In particular, the benzylic C-H bonds have been gentle to extremely active, and distinctive transformations have been extended from aryl/diaryl methane in recent past years\cite{3}. However, the most industrial synthesis of pharmaceutical intermediates and fine chemicals have been delivered to the derivative of diphenylmethane compounds\cite{4}. Hence, the various benzylic derivatives, such as a easily leaving groups, acetates\cite{5}, mesylates\cite{6}, tosylates\cite{7}, phosphate\cite{8}, carboxylates \cite{9}, sulfonates\cite{10}, N,N-ditosylbenzylamines\cite{11} and more recent 1-alkoxy-1\textit{H}-benzotriazoles\cite{12}, has been applied successfully in Pd mediated cross-coupling reaction with aryl boronic acid (scheme 1). Yi et al.,\cite{13} Shi et al.,\cite{14} and his co-workers have been recently exposed limited reactivity in imperfect transformations of benzyl alcohol via Ru and Pd catalyst in the absence of the base. The applications of alcohols are incomplete in cross-coupling reactions by employing C-O electrophiles. It can be transported as one of the most plenteous basic units in lignin\cite{15}. Although these reactions are majorly focused on Friedel-Crafts alkylation which offered exact conditions via carbocation mechanism by using Lewis acid catalyst\cite{16}. Therefore, the earth-
profuse first-row transition metal, for example, iron, revealed more attractive for their apparent advantages, high abundance on earth, cut-rate, low or non-toxic, and distinctive catalytic activities\textsuperscript{[17]}. The Lewis acidity of iron various from diffident to very high, this property is efficiently correlated with the oxidation state and after this is tunable by excellent ligands\textsuperscript{[18]}. Although iron-catalyzed reactions of the Friedel-Crafts are embedded, the prominent Lewis acidity of high-valent iron still provides enough space for discovery\textsuperscript{[19]}. Some of the few heterogeneous catalyst systems had been employed the C-O bond activation\textsuperscript{[20]}.

![Scheme 1](image)

**Scheme 1** 8wt%Fe/SBA-15 catalyzed towards $sp^3$ C-O bond activation of benzylic alcohol and aryl boronic acid.

However, the direct catalytic transformation of benzylic alcohols via the heterogeneous system, remained challenging due to the inertness of their C-O bond via C-C coupling transformation and the acidity of OH. Indeed, heterogeneous catalysts with such activity for the straightforward synthesis of a diarylmethane by the base and additive free dehydrogenative coupling of benzylic alcohols with aryl boronic acid are rare and very limited.

Recently, we reported a heterogeneous iron catalyst such as 8wt%Fe/SBA-15 for cross-dehydrogenative arylation of biphenyl methane C($sp^3$)-H with an aren and arylation of benzene C($sp^2$)-H by using various aryl boronic acids\textsuperscript{[21]}. The reaction involves a formation of Fe(IV) species via single electron transfer (SET), as a key intermediate derived from the benzylic cation, where react with arene followed by Friedel-Craft alkylation product. We made another reaction to ensure the iron (IV) formation aryl boronic acid reaction with aren undergoes oxidative C-H bond activation via SET (Single electron transfer) to give the coupled product. In work,
we summarize the recent efforts toward C-O bond activation via heterogeneous 8wt%Fe/SBA-15 catalyzed in the absence of the base and additive. The benzylic alcohols persisted also proficiently activated by 8wt%Fe/SBA-15 to generate benzylic cation intermediates, via the elimination of the hydroxy group, which was coupled with nucleophiles, such as boronic acids.

The catalyst 8wt%Fe-SBA-15 has been already discussed in previous reports, [21] by using XRD, N₂ adsorption isotherm, EPR, DRS-UV, HR-TEM, and TPR. Here, we have been examined the acidic property of iron grafting over mesoporous silica (SBA-15) surface by using the NH₃-TPD. It has been used extensively in both quantify and differentiate the acid sites of synthesized catalyst structures [22]. Because of its high reactivity beside surface structures through hydrogen bonding and coordination, it usually produces presence of the catalyst acidity [23]. However, its average kinetic diameter (7.26 nm) allows it to access almost all sites.

Figure 1 contains TPD results of 8wt%Fe-SBA-15 along with total acidity counts.

Figure 1. NH₃-TPD profiles of 8 wt%Fe-SBA-15 prepared by grafting of Fe³⁺ by using the selective extraction deposition (SED) technique.
Table 1: Optimization reaction condition on benzyl alcohol with phenyl boronic acid.

\[
\begin{align*}
&\text{Entry} & \text{Catalyst (100mg)} & \text{Solvent} & \text{Temperature} & \text{Time} & \text{Yield (%)\(^{(a)}\)} \\
1 & 8\text{wt\% Fe/SBA-15} & \text{THF} & 80^\circ\text{C} & 24h & 30\% \\
2 & 8\text{wt\% Fe/SBA-15} & \text{THF} & 80^\circ\text{C} & 48h & 35\% \\
3 & 8\text{wt\% Fe/SBA-15} & \text{Dioxane} & 80^\circ\text{C} & 24h & - \\
4 & 8\text{wt\% Fe/SBA-15} & \text{Acetonitrile} & 80^\circ\text{C} & 24h & - \\
5 & 8\text{wt\% Fe/SBA-15} & \text{DBE} & 80^\circ\text{C} & 24h & - \\
6 & 8\text{wt\% Fe/SBA-15} & \text{EtOAc} & 80^\circ\text{C} & 24h & - \\
7 & 8\text{wt\% Fe/SBA-15} & \text{Benzyl alcohol} & 80^\circ\text{C} & 24h & - \\
8 & 8\text{wt\% Fe/SBA-15} & \text{DMF} & 80^\circ\text{C} & 24h & - \\
9 & 8\text{wt\% Fe/SBA-15} & \text{DCE} & 80^\circ\text{C} & 24h & 25\% \\
10 & 8\text{wt\% Fe/SBA-15} & \text{DCE} & 110^\circ\text{C} & 24h & 40\% \\
11 & 8\text{wt\% Fe/SBA-15} & \text{THF} & 110^\circ\text{C} & 24h & 45\% \\
12 & 8\text{wt\% Fe/SBA-15} & \text{DCE} & 110^\circ\text{C} & 24h & 50\% \\
13 & 8\text{wt\% Fe/SBA-15} & \text{DCE} & 130^\circ\text{C} & 10h & 70\% \\
14 & 4\text{wt\% Fe/SBA-15} & \text{DCE} & 130^\circ\text{C} & 10h & 50\% \\
15 & 2\text{wt\% Fe/SBA-15} & \text{DCE} & 130^\circ\text{C} & 10h & 45\% \\
16^{(a)} & 8\text{wt\% Fe/SBA-15} & \text{DCE} & 130^\circ\text{C} & 10h & 50\% \\
17^{(b)} & \text{AlCl}_3(10\text{mol\%}) & \text{DCE} & 130^\circ\text{C} & 10h & \text{Trace} \\
18^{(c)} & - & \text{DCE} & 130^\circ\text{C} & 10h & - \\
19^{(d), (f)} & \text{8wt\% Fe/SBA-15-Benzyl alcohol} & \text{DCE} & 130^\circ\text{C} & 10h & \text{Reactant Remaining (benzyl alcohol)-GC-MS [conversion 0%],} \\
& \text{8wt\% Fe/SBA-15-phenyl boronic acid} & \text{DCE} & 130^\circ\text{C} & 10h & \text{Reactant converted to (phenyl boronic acid trimer)-GC-MS [conversion 100%]} \\
20^{(e), (f)} & - & \text{DCE} & 130^\circ\text{C} & 10h & - \\
\end{align*}
\]

\text{Reaction conditions: 1 (0.3 mmol), 2 (0.9 mmol) and catalyst (8wt\%Fe/SBA-15) (100mg) in DCE (2 mL) was stirred at 130^\circ\text{C} for 10h under N}_2\text{ atmosphere. (a) 1 (0.9mmol) (b) 10 mol\%AlCl}_3\text{ (c) Without catalyst. (d) Only one reactant 1 (0.3mmol). (e) Only one reactant 2 (0.9mmol). (f) Conversion monitored by GC-MS (g) Isolated yield.}

Therefore, it is significant to regulate the amount of acid site present on the catalyst surface. It was the apparent shift from the grafted iron on the mesoporous silica surface, with the total acidity after grafted over mesoporous silica is 0.135 mol/g, and shows the three different desorption peaks are derived from the TPD analysis. Based on the temperature it showed three active acid sites such as weak,
moderated, and strong acid sites respectively were shown in Table S1. The first desorption peak at 271°C has been ascribed previously to under coordinated weak Lewis acidic Si-Fe-OH, and it has been suggestively attenuating upon SBA-15 deposition [24]. The second desorption peaks at 476°C has been assign moderated acid site its belong to coordinate the Fe-O-Si of in the mesopore region of SBA-15[25]. While there was evidence for desorption peak at 624°C, it corresponds to the strong Lewis acid site present in the Fe-O-Si of micropore region of mesoporous silica (SBA-15) [26]. While we do not wish to disperse a molecular structure of amorphous 8wt%Fe-SBA-15, and some zeolites display features in this temperature regime and the usual attribution is to Bronsted acid sites [27]. Therefore, overhead acidity results suggest that the selective of the grafting process(SED), which allowed for the most sites to be grafted by iron. Hence, the above three different strength of acid site could be employed the better catalytic activity for the sp3 C-O activation reactions.

We began our studies by examining the reaction of benzylation of phenylboronic acid with benzyl alcohol in the absence of a base, and additives the results are shown in Table 1. This reaction carried to optimize the reaction conditions, various solvents, and reaction temperature. The activity results suggest that 8wt%Fe/SBA-15 catalyst showed a yield of 3a 30% (Table 1, entry 1). As we expected, increase the time, and change the solvents the yield of the reaction was high but actual results reverse. Nature of the solvents playing an important role in this reaction. (Table 1, entry 2-8) The reaction yield was improved from 40% to 50% by increasing the temperature from 110°C to 130°C (Table 1, entry 9-12). Inspired by the reports on the C-O bond cleavage reaction, to generate the benzylic cation species from the benzyl alcohol, the reaction temperature change must be increased. [20c] Besides, 70% yield of 3a was obtained when the temperature was increased to 130°C (Table 1, entry 13). Hence, we fixed this entry as an optimal set of reaction condition. Thus, we are screening with various loading iron supported on mesoporous silica (SBA-15) catalyst it gave (45-50%) (Table 1, entry 14,15). Next, we examined the stoichiometry of benzyl alcohol, it gave 50% yield. (Table 1, entry 16). When using 10mol% AlCl3 catalyst, it gave trace amount product, i.e. no product formation which was used the reaction without a catalyst. (Table 1, entry 17,18) Even though the reaction has been examined without phenylboronic acid,
the results showed no conversion from the benzyl alcohol. Furthermore, have been ventured including the absence of benzyl alcohol it produced only boronic trimer from boronic acid, GC-MS monitored these results. (Table 1, entry 19,20).

Further, we analyzed with the general applicability of the optimized system, a variety of substituted aryl boronic acid derivatives for diarylmethane synthesis by using benzylic alcohol 1a (Table 2).

Table 2: Cross-coupling of benzyl alcohol with various aryl boronic acids. (a)

![Chemical structures and yields](image)

We have noticed that functionalities, such as 4-methoxy and 4-methyl, as well as halide substituents on the benzylic group of benzyl alcohol, are well tolerated and gave a (55-65%) yield of diphenylmethane derivatives (Table 2, 3a-3l). Further, Also, we examined the tolerance of the benzyl alcohol derivatives react with phenylboronic acid, it provides the isolated yield (50-65%) (Table 3, 5a-i). Therefore, based on the above experiences, it is anticipated that reaction may proceed within iron assisted carbocation mechanism via Friedel craft alkylation reaction (Scheme 2). In the first step of the reaction, weak Lewis base of benzyl
alcohol (1A) adsorbed active on the catalyst surface to form 4A, generate the partial deprotonation from the benzyl alcohol. Next step, attack the nucleophile of phenylboronic acid (2A) to the intermediate 4A, then it converts to another intermediate 5A. In the final step, the elimination of B(OH)3 to form a 6A, finally it generates the partially benzylic cation and phenyl anion via alkylation to form a product (3A).

Table 3: Cross-coupling of various benzyl alcohol with phenyl boronic acid. (a)

In conclusion, we have been developed the first heterogeneous iron-based such as 8wt%Fe-SBA-15 catalyst to construct diphenylmethane via sp3C-O bond activation of aromatic benzylic alcohol reacts with aryl boronic acid reaction in the absence of base or additive. The highlight of the design is that it employs a simple heterogeneous iron catalyst. The catalyst could be recycled for five runs without loss of activity. Furthermore, the iron-catalyzed C-C reaction coupling can be recognized under gram-scale in synthetically satisfying yield. Further studies toward the development of new C-O activation reactions of benzylic alcohol are currently underway in our laboratory.
Scheme 2. Proposed mechanism for 8wt%Fe/SBA-15 catalyzed sp3 C-O bond activation of benzylic alcohol and aryl boronic acid.

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