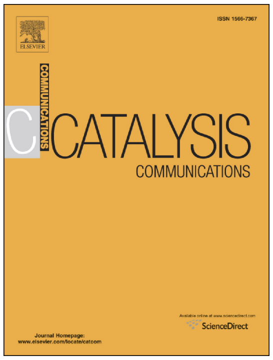

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Synthesis of Internal Olefins by Direct Coupling of Alcohols and Olefins over Moβ Zeolite[†]

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[†] IICT-Manuscript communication number: IICT/Pubs./2018/335

Abstract

An efficient and novel Moβ zeolite catalyzed sp^2-sp^3 C-C bond development reaction over the direct coupling of alcohols and alkenes has been performed in solvent free environment. The current method gives an attractive access to a wide variety of polysubstituted alkenes in good to excellent yields. The Moβ zeolite was effectively reused for up to 5 successive cycles.

Keywords: Alkenes, Alcohols, Cross-Coupling, Internal alkenes, Zeolites

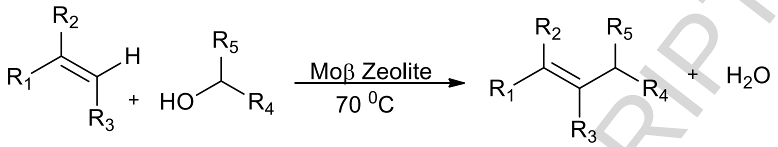
1. Introduction

The development of C(sp^2)-C(sp^3) bond-construction reaction is one of the vital reactions in modern synthetic organic chemistry [1]. Traditionally, various protocols for the construction of sp^2-sp^3 C-C bonds were developed with various coupling reactions such as Heck, Stille, Hiyama and Negishi coupling [2-7]. However, the requirement of additional synthesis steps for the effective precursors, use of expensive/toxic homogenous catalysts, formation of stoichiometric amounts of wastes, requirement for functionalized starting materials make such a method justly unattractive. Hence, there is a solid requirement for establishing methodologies for the construction of sp^2-sp^3 C-C bonds which includes the straight coupling of alcohols and olefins due to its environmentally friendly and atom-efficient nature because only water is produced as a side product [8-10]. Currently, very few protocols for the straight coupling of alcohols and alkenes to develop sp^2-sp^3 C-C bonds were reported [11-20]. However, most of these protocols have one or more drawbacks like use of expensive Pd catalysts [11,12], toxic halogenated solvents like 1,2-dibromoethane, dichloromethane, and dichloroethane [13-16,18, 20] and homogeneous catalysts [17]. Therefore, there is a solid need for advancement of polysubstituted olefins from alkenes with alcohols using heterogeneous catalysts under solvent free environment where the catalyst possibly simply recoverable and reused with no significant damage in their catalytic activity.

In the past decade, solvent-free synthesis is an important part of green chemistry because of its distinct advantages such as eliminates the use of toxic organic solvents, reduces pollution and costs, requires less energy, faster reaction rates, reduction in reactor size, simplicity in process and handling, which are especially important in industry [21-22].

Zeolites are crystalline microporous aluminosilicates with pore structures consisting of a three dimensional (3D) network of SiO_4 and AlO_4 tetrahedra linked by corners sharing oxygen ions [23]. Catalysts supported by different zeolites have played a significant role in both fine chemical and petroleum industries because of their exclusive physical and chemical properties, like high internal surface area, uniform channel size, strong acidity and good thermal/hydrothermal stability, and unique molecular shape selectivity [24-25]. Among various types of zeolites, Beta (β) has shown a flexible catalytic material for various applications in industry [26]. Zeolite β exists of an intergrowth of two or more polymorphs comprised of a 3D system of 12-membered ring channels with pore diameters of 0.55 × 0.55 nm and 0.76 × 0.64 nm [27]. In recent years, catalysis supported by metal modified zeolite β attracted much attention due to the large-pore channel system, large available micro-pore volume, eco-friendly nature, high surface area, chemical and thermal stability, and the existence of active sites in various concentrations which are helpful in a variety of acid-catalyzed reactions [28-34].

In extension of our interest towards the expansion of new and efficient synthetic methods using zeolites [35-37], herein we wish to account the first example of zeolite catalyzed highly regio- and stereoselective dehydrative cross-coupling of olefins with alcohols in solvent free conditions, where water is the single by-product (Scheme 1). The definite goals of this protocol are to 1) determine the best zeolite and metal modified zeolite catalyst for the coupling reaction, 2) evaluate the effect of amount of catalyst, reaction temperature, reaction time, and mole ratio of alkene to alcohol on the yield of coupling product, 3) check the possibility and limitations of the reaction with different olefins and alcohols, 4) determine significant reaction route that leads to coupling products, and 5) estimate the stability of catalyst over 5 cycles.



Scheme 1. Synthesis of Internal Alkenes.

2. Experimental Section

2.1. Synthesis of 10%Moβ zeolite

The zeolite $NH_4\beta$ was calcined at 500^{o}C for 10 h to acquire zeolite HBeta (Hβ). Moβ was synthesized using the modified impregnation method. Zeolite Hβ (2g) was added to the aqueous solution of Mo precursor (368.05 mg of ammonium molybdate which contains 200 mg of Mo was dissolved in 5 mL distilled water), then it was mixed homogenously with glass rod and was placed on hot plate at 100 ^{o}C to remove excess water for 1 h. After impregnation, the catalyst was dried overnight at 100 ^{o}C and calcined at 450 ^{o}C for 6 h in the presence of static airflow before using it for the reaction. The other metal modified zeolites (Snβ, Feβ, Coβ, Crβ, and Wβ) were synthesized using same procedure stated above.

2.2. Experimental procedure

10% Moβ zeolite (100 mg) was introduced to the well stirred solution of vinylarene (1 mmol) and alcohol (0.8 mmol) in a 15 mL of sealed vial and the reaction mixture was allowed to stir at 70 °C. After disappearance of the substrate (monitored by TLC) or after an appropriate time, the reaction mixture was cooled to room temperature, diluted with ethyl acetate. The catalyst was removed by filtration, rinsed with ethyl acetate and removal of solvent in vacuo yielded a crude residue. The crude residue was further purified by column chromatography on silica gel (230-400 mesh) using ethyl acetate/hexane as eluent to afford pure products. All the products were identified on the basis of NMR spectral data and quantified using gas chromatography. More details on catalyst characterization and analytical procedures are provided in supporting information.

3. Results and Discussion

3.1. Catalyst characterization

XRD studies revealed that no considerable modifications take place in the crystallinity of the supported Hβ zeolite throughout the catalyst preparation process (Figures S1 and S2). The outcome from FT-IR spectra of Hβ, and 10% Moβ zeolites indicate that Hβ was resistant throughout the preparation of catalyst (Figure S3). The TEM image of 10% Moβ shows a uniform and dense dispersion of the nano-sized particles of molybdenium oxide (2–8 nm) on the surface of Hβ (Figure S4). The narrow scan of Mo(3d) on as-synthesized 10% Moβ shows binding energy peaks at 233.37 and 236.64 eV, which are typical values of the 3d orbital doublet of Mo^{6+} (Figure S5).

Temperature programmed desorption of ammonia (NH_3-TPD) has been performed on the zeolites and metal modified β zeolites to determine the strength and amount of acid sites (Table

Table 1 Acidity of Hβ and metal modified β zeolites

Catalyst	Acidity[a] (mmol/g)	Acidic sites distribution[b]		
		LT-peak[c]	MT-peak[c]	HT-peak[c]
Hβ	1.134	42.9	42.1	15.0
10% Moβ	1.539	47.9	35.9	16.2
10% Snβ	1.222	33.5	35.5	31.0
10% Feβ	1.161	35.1	52.2	12.7
10% Wβ	1.398	30.8	51.1	18.1
10% Crβ	1.223	34.3	65.7	-
10% Coβ	1.453	34.1	36.3	29.6
2% Moβ	1.167	40.7	43.9	15.4
5% Moβ	1.288	45.0	39.7	15.3

[a] Total acidity amount determined by NH_3-TPD. [b] The NH_3-TPD (%) distribution of acidic sites. [c] LT-peak represents weak acid sites (150-250 °C), MT-peak represents medium acid sites (250-550 °C) and HT-peak represents strong acid sites (550- 650 °C).

1, Table S2, Figure 1, Figure S6, and Figure S7). As can be seen in Table 1, the introduction of metal cation on Hβ zeolite leads to increase in the amount of acid sites. Among the modified Hβ zeolites, Moβ was found to have more number of acid sites present on the catalyst surface. As the amount of Mo content increased from 2% to 10%, the amount of acid sites increased (Table 1, Figure S6).

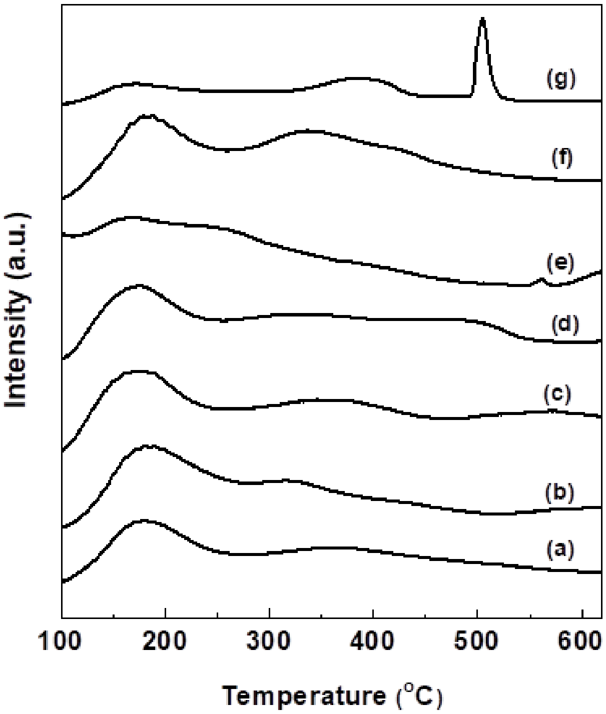


Figure 1. NH_3-TPD profile of a) Hβ, b) 10%Moβ, c) 10%Snβ, d) 10%Feβ, e) 10%Wβ, f) 10%Crβ, g) 10%Coβ.

3.2. Optimization of the reaction conditions

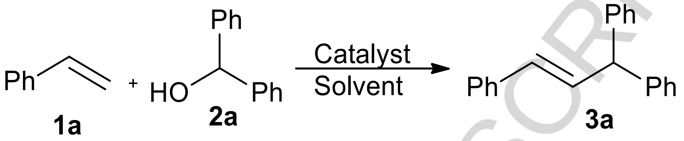
*3.2.1. Effect of different catalysts on coupling reaction of styrene (**1a**) with benzhydrol (**2a**)*

Initially, we investigated the direct cross-coupling reaction with styrene (**1a**) and benzhydrol (**2a**) as the model substrates to optimize the various conditions of the reaction (Table 2 and S3). To select the foremost catalyst, initially the reaction was tested with montmorillonite

K10, MCM-41, and various zeolites in sealed tube at 70 °C for 4 h (Table 2, entries 1-7). Besides Montrimorillonite K10 and Hβ, other catalysts such as MCM-41, H-Mordenite, HZSM-5, HY, and NaY did not or only sluggishly catalyzed the coupling reaction towards the corresponding product **3a**. Compared to the examined catalysts, Hβ exhibit the highest catalytic activity and provided the corresponding coupling product in 67% yield because of large pore size and strong acidic sites (Table 2, entry 7) [27]. No conversion was detected in the absence of catalyst (Table 2, entry 8).

The examination of various solvents with Hβ catalyst revealed that the performance of the reaction in solvent free condition was considerably better compared to DCE, DCM, $CHCl_3$, toluene, H_2O, and CH_3CN (Table 2, entries 9-14). Later, we concentrated on gaining the highest yield of **3a**, and examined direct dehydrative cross-coupling of **1a** with **2a** using different metal modified zeolite β catalysts (Table 2, entries 15-20). The results showed that the reaction with Moβ zeolite exhibits best catalytic activity (gave the corresponding product in 83% yield and 87% selectivity) compared to other metal exchanged zeolite Hβ due to more number of acid sites present on the catalyst surface (Table 2, entry 15). Results also showed that the order of reactivity was Mo > Sn > Fe > Co > W > Cr. It is known that the modification of metal in zeolites influences the strength of acid site, total acidity, and acid sites nature [37] (Table 1). As can be seen from Table 1, the presence of more number of acid sites are responsible for the high catalytic activity of 10% Moβ, where as other metal modified beta zeolites have less number of acid sites which gave less catalytic activity. We had also investigated the cross-coupling of **1a** with **2a** using Moβ catalyst with different Mo loadings (2, 5, 7, 10, and 12 wt%) (Table 2, entries 21-24). Yield of **3a** was raised from 66 to 83 % with raise in Mo content from 2 to 10 wt%. Whereas further increase in Mo loading did not show any considerable modification in the yield of **3a**. This is due to the increase in the number of acid sites with raise in Mo content from 2 to 10 wt% (Table 2, Figure S6). The catalytic activity depends on many factors like amount of total acid sites, surface area, pore size, and Si/Al ratio and it is difficult to clearly correlate all the properties of the catalyst tested with the catalytic performance. The amount of total acid sites can only be correlated to the catalytic activity in this study.

Table 2 Optimization of reaction conditions[a]



Entry	Catalyst	Solvent	Yield[b] (%)
1	HMCM-41	-	4
2	Montmorillonite K10	-	38
3	H-Mordenite	-	6
4	HZSM-5 (40)	-	0
5	HY	-	4
6	NaY	-	0
7	Hβ	-	67
8	Without catalyst	-	0
9	Hβ	DCE	61
10	Hβ	DCM	44
11	Hβ	$CHCl_3$	21
12	Hβ	Toluene	14
13	Hβ	H_2O	<5
14	Hβ	CH_3CN	0
15	10% Moβ	-	83
16	10% Snβ	-	48
17	10% Feβ	-	35
18	10% Coβ	-	24
19	10% Crβ	-	7
20	10% Wβ	-	18
21	2% Moβ	-	66
22	5% Moβ	-	74
23	7% Moβ	-	78
24	12% Moβ		82

[a] Reaction conditions: **1a** (1 mmol), **2a** (0.8 mmol), catalyst (100 mg), solvent (2 mL), 70 °C, 4 h, sealed vial. [b]Isolated yields based on **2a**.

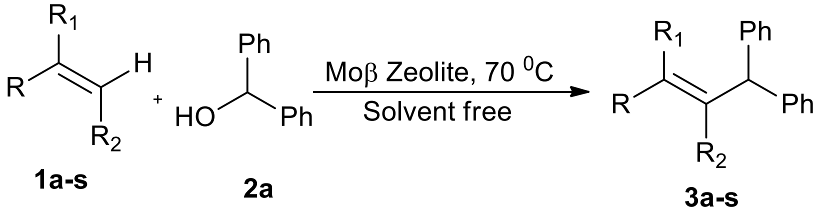
3.2.2. Effect of amount of Moβ, temperature, reaction time and mole ratio on coupling reaction

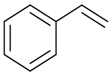
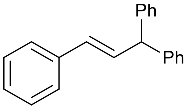
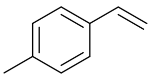
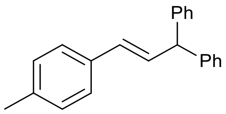
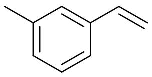
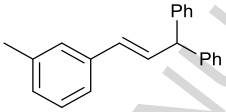
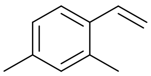
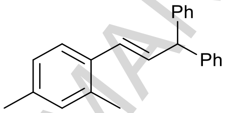
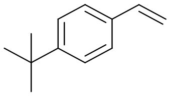
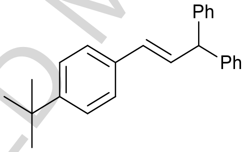
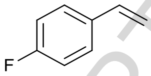
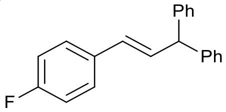
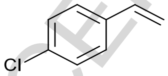
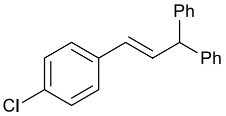
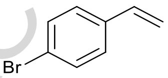
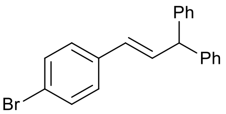
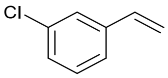
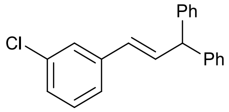
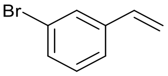
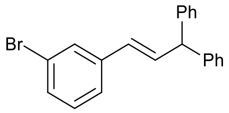
Once 10% Moβ was confirmed as the best catalyst for direct cross-coupling reaction of **1a** and **2a**, the influence of amount of catalyst, reaction temperature, reaction time, and mole ratio of **1a** and **2a** were studied (Table S3). With increase in the amount of catalyst from 25 to 100 mg, the yield of **3a** was raised from 42 to 83%. Whereas, further increase in the amount of catalyst from 100 to 125 mg has not shown any notable change in the yield of product **3a** (Table S3, entries 1-5). The same trend was observed with increase in reaction temperature and the reaction time (Table S3, entries 6-12). The mole ratio of **1a** to **2a** also had a accountable influence on the yield of **3a**. While increase in the mole ratio of **1a** to **2a** (1:0.5 to 1:0.8), the yield of **3a** was increased from 73 to 83% (Table S3, entry 13 and 4). Whereas further increase in the mole ratio of **1a** to **2a** (1:0.8 to 1:1 and 1:1.2), the yield of **3a** was reduced from 83 to 71 and 68% due to the formation of ether as a side product (Table S3, entries 14-15). From the above acquired data, it can be confirmed that the optimized reaction parameters to obtain the best yield for this direct cross-coupling reaction are 1:0.8 mole ratio of **1a** to **2a** at 70 ^{o}C over 10% Moβ catalyst (100 mg).

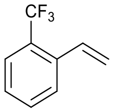
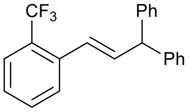
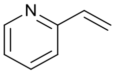
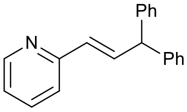
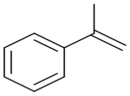
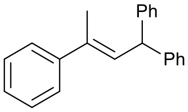
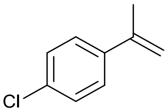
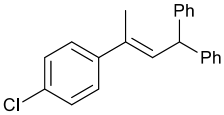
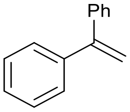
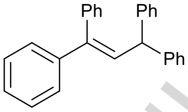
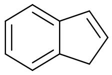
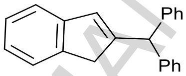
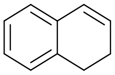
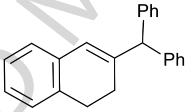
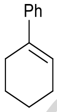
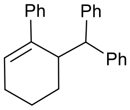
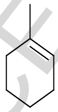
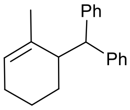
*3.3. Moβ catalyzed direct coupling reaction of **2a** with various olefins*

Based on the optimized parameters, the possibility and limitations for the reaction of different olefins with **2a** were examined (Table 3). Along with **1a**, a set of substituted styrenes consists of both electron-rich or electron-deficient groups were all appropriate reactants, and produced the subsequent coupling products in excellent yields (Table 3, entries 1-11). The sterically hindered disubstituted aromatic alkenes like prop-1-en-2-ylbenzene, 1-chloro-4-(prop-

Table 3 Olefin variation[a]



Entry	Olefin	Product	Time (h)	Yield[b] (%)
1	 **1a**	 **3a**	4	83
2	 **1b**	 **3b**	3	86
3	 **1c**	 **3c**	3	85
4	 **1d**	 **3d**	3	88
5	 **1e**	 **3e**	3	78
6	 **1f**	 **3f**	4	78
7	 **1g**	 **3g**	4	78
8	 **1h**	 **3h**	4	80
9	 **1i**	 **3i**	6	70
10	 **1j**	 **3j**	6	76

11	 **1k**	 **3k**	6	73
12	 **1l**	 **3l**	12	00
13	 **1m**	 **3m**	2	89
14	 **1n**	 **3n**	2	88
15	 **1o**	 **3o**	2	91
16	 **1p**	 **3p**	3.5	90
17	 **1q**	 **3q**	3.5	87
18	 **1r**	 **3r**	6	85
19	 **1s**	 **3s**	6	70

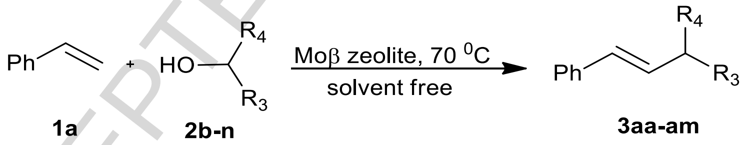
[a] Reaction conditions: **1a-s** (1 mmol), **2a** (0.8 mmol), 10% Moβ (100 mg), 70 °C, sealed vial. [b] Isolated yields based on **2a**.

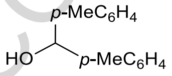
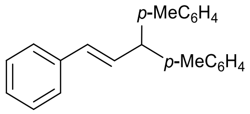
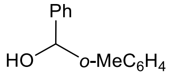
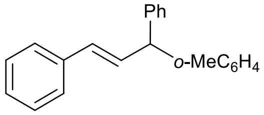
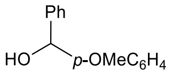
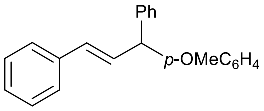
1-en-2-yl)benzene (**1m** and **1n**) and ethene-1,1-diyldibenzene (**1o**) were also well tolerated in this method, leading to the preferred products in excellent yields (Table 3, entries 13-15). Additionally, cyclic internal olefins, such as indene (**1p**) and 1,2-dihydronaphthalene (**1q**) were also exhibited excellent activities (Table 3, entries 16 and 17). Especially, due to the high steric hindrance, reaction of 1-phenyl-1-cyclohexene (**1r**) and 1-methyl-1-cyclohexene (**1s**) offered the more stable trisubstituted olefins **3r** and **3s** by the selective β-H elimination (Table 3, entries 18 and 19).

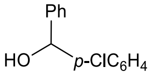
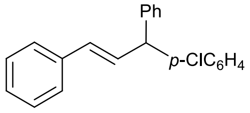
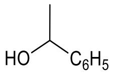
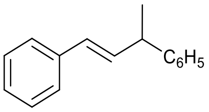
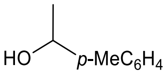
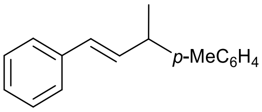
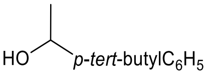
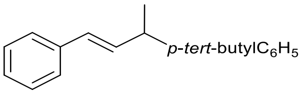
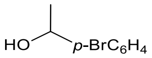
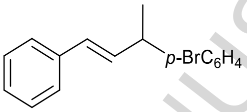
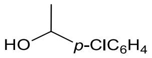
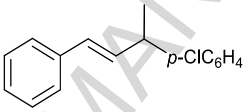
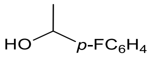
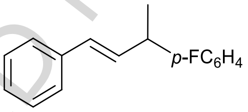
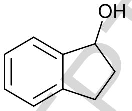
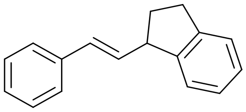
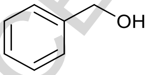
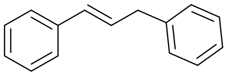
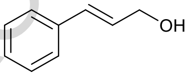
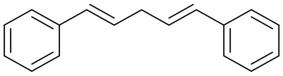
3.4. Moβ catalyzed direct coupling reaction of styrene with various alcohols

The scope and limitations of the 10% Moβ catalyzed direct coupling reaction was further extended to a variety of alcohols (Table 4). It is observed that benzhydrol having electron-donating groups (-Me and -OMe) and halo group (-Cl) on the aryl ring were furnished the subsequent products in good to excellent yields (Table 4, entries 1-4). 1-Phenylethanol and its derivatives bearing electron-donating groups (-Me and -*tert*-butyl) and halo groups (-Br, -Cl and –F) on the aryl ring were also gave the relevant products in good to excellent yields (Table 4, entries 5-10). In addition, cyclic alcohol i.e. 1-indanol (**2l**) afforded the preferred product in moderate yield (Table 4, entry 11). However, benzyl alcohol (**2m**) and cinnamyl alcohol (**2n**) were unable to generate the corresponding products in the optimized reaction parameters (Table 4, entries 12 and 13).

Table 4 Alcohol variation[a]



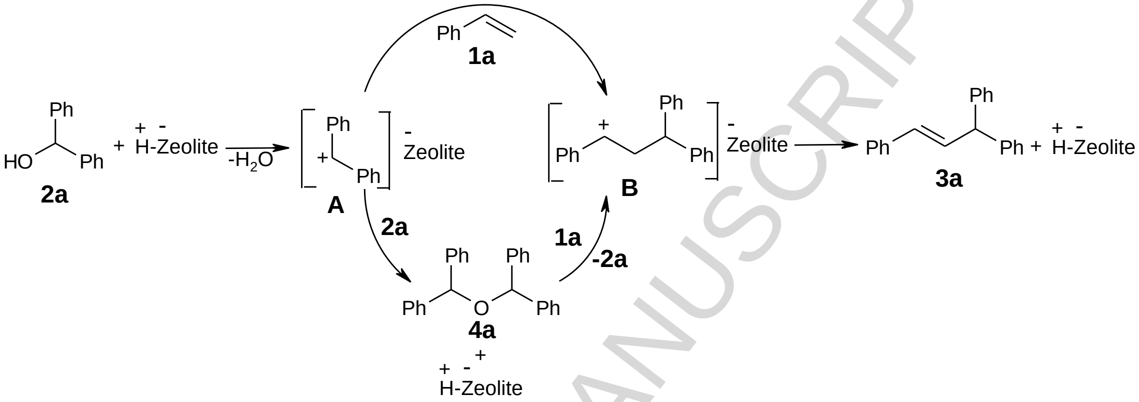
Entry	Alcohol	Product	Time (h)	Yield[b] (%)
1	 **2b**	 **3aa**	3	80
2	 **2c**	 **3ab**	5	64
3	 **2d**	 **3ac**	3	78

4	 **2e**	 **3ad**	3	80
5	 **2f**	 **3ae**	4	61
6	 **2g**	 **3af**	4	78
7	 **2h**	 **3ag**	4	76
8	 **2i**	 **3ah**	5	75
9	 **2j**	 **3ai**	5	76
10	 **2k**	 **3aj**	5	70
11	 **2l**	 **3ak**	4	57
12	 **2m**	 **3al**	12	00
13	 **2n**	 **3am**	12	00

[a] Reaction conditions: **1a** (1 mmol), **2b-n** (0.8 mmol), 10% Moβ (100 mg), 70 °C, sealed vial. [b] Isolated yields based on alcohol.

3.5. Reaction mechanism

In order to obtain clear mechanistic insights into this reaction, few control experiments were performed (*see* supporting information). Based on the findings and literature study [12-17], two possible routes for this coupling reaction are recommended (Scheme 2). One possible route could be a direct alkylation of **1a** with carbocation intermediate (**A**) (which is initially generated by activation of **2a** using zeolite) to produce carbocation intermediate (**B**), followed by deprotonation to provide the desired product **3a**. Another probable pathway is the generated carbocation intermediate (**A**) reacts with **2a** to form the corresponding dimeric ether (**4a**). The ether **4a** next reacts with **1a** to generate the corresponding product **3a** and along with alcohol **2a**.



Scheme 2. Plausible mechanism for the direct coupling of olefins with alcohols.

To regenerate, the 10% Moβ was filtered to separate from the reaction mixture and washed with ethyl acetate, dried at 100 ^{o}C for 8 h and calcined at 450 ^{o}C. Recyclability of the 10% Moβ catalyst was tested by performing the reaction of **1a** with **2a** in optimized reaction parameters (Table S4). The recycled 10% Moβ catalyst exhibit constant activity up to five cycles.

4. Conclusions

Briefly, we have developed the first example of zeolite catalyzed dehydrative cross-coupling of alkenes and alcohols in solvent free environment. The current method presents an attractive way to a wide variety of polysubstituted alkenes in good to excellent yields.

Acknowledgements

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- Moβ zeolite exhibits best catalytic activity towards the synthesis of internal olefins.
- The products obtained in moderate to excellent yields under solvent free conditions.
- The reused catalyst showed consistent activity up to five cycles.