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Rh-catalyzed 1,4-addition reactions of arylboronic acids accelerated by coimmobilized tertiary amine in silica mesopores



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ABSTRACT

Mesoporous silica-supported Rh complex catalysts were prepared by simple silane-coupling, followed by complexation, and characterized by FT-IR, SEM, Rh K-edge XAFS, and elemental analysis. Local structures of the Rh complexes in each sample were almost similar to those of a nonporous silica-supported diaminorhodium complex. Co-immobilization of a tertiary amine on the same silica surface induced slight changes to the Rh complex structure in the case of the support with smaller pores. The prepared catalysts showed high activity for the 1,4addition reaction of phenylboronic acids. Co-immobilization of the tertiary amine increased the reaction rate by more than 7-fold, with turnover number of nearly 8500. The catalytic performance achieved with this novel system is with much higher than that reported previously with a nonporous silica-supported catalyst. The mesoporous silica-supported Rh complex-tertiary amine showed a wide substrate scope, including unsaturated ketones and nitriles. This co-immobilized tertiary amine may activate phenylboronic acid to enhance its reactivity in the transmetalation step with Rh-OH species.

1. Introduction

Concerted catalysis by two isolated functional groups embedded on a solid surface offers highly efficient approaches in organic synthesis [1]. Catalytic nucleophilic additions, such as aldol and Henry reactions, on silica surfaces bearing both acidic functionalities and basic amines have received considerable attention due to the excellent catalytic performance of the embedded moieties [2]. This cooperative strategy has been recently extended to the synthesis of fine chemicals using metal complexes as immobilized active centers [3]. For example, Córdova et al. reported efficient asymmetric cascade transformations via catalysis on silica surface containing a Pd complex and a secondary amine [3d]. Fernandes et al. demonstrated the superior catalytic oxidations of alcohols to aldehydes using a click chemistry immobilized Cu complex via cooperative action with the co-immobilized TEMPO [3f].

With continued exploration in this area of catalysis, understanding the effects of the support structure on such cooperative catalysis by more than two functionalities is the next research frontier. For acidamine cooperativity, Jones et al. investigated the effect of mesopore size on aldol-type condensation reactions [4]. Although concerted catalysis using metal complexes on solid supports is one of the most actively pursued topics in the field of heterogeneous catalysis, the precise effect of the support on such cooperativity is still unclear. Our group recently reported the allylation of nucleophiles by concerted catalysis between a precisely designed Pd complex and a tertiary amine [5]. While this cooperative phenomenon was observed initially on a nonporous silica surface, the catalytic performance increased significantly in silica mesopores [6]. Detailed characterization of the Pd complex indicated no significant change in its local coordination structure, suggesting that the enhanced cooperativity between Pd complex and amine in the mesopores results from the different environments of their distance and/or direction from nonporous surface [6]. Encouraged by these findings, we expanded our studies on cooperative catalysis in mesopores to other metal complex-catalyzed reactions and the results herein.

Rh-catalyzed 1,4-addition is one of the most powerful strategies for

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Scheme 1. MS/diamine/Rh/NEt $_2$ -catalyzed 1,4-addition reactions of arylboronic acid.

Та	ble	1
Ta	ble	1

Physicochemical properties of synthesized MS supports.

MS Support	Surface area $[m^2g^{-1}]^a$	Pore size [nm] ^b	Pore vol. [ml/g] ^b
MS(C8)	1865	1.6	1.46
MS(C12)	1175	2.3	1.01
MS(C18)	876	3.1	1.01

 $^{\rm a}$ Determined by N_2 adsorption-desorption isotherm measurement. $^{\rm b}$ Determined by BJH method.



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the synthesis of β -arylcarbonyl compounds. Following the seminal report by Miyaura et al. in 1997 [7], various novel homogeneous [8] and heterogeneous Rh catalysts [9] have been developed for this transformation. Shimazu et al. reported a heterogeneous NiZn/Rh catalyst containing a Rh aqua complex and hydroxide ions in the NiZn interlayer space [9k]. Our group also reported a nonporous silica-supported Rh complex and tertiary amine system for the 1,4-addition reaction [10]. "Double-activation catalysis" by Rh and basic functionalities is the key step in such heterogeneous catalytic systems which activates the phenylboronic acid by formation of the tetra-coordinated boron species, resulting in an accelerated C–B bond cleavage and faster transmetalation between Rh – OH and Ph-B [10]. Based on this mechanistic rationale, changes in the location of the Rh complex and the basic site, such as immobilized amine, should have a marked effect on its catalytic performance.

We report here our studies on the development of an efficient 1,4addition reaction of arylboronic acid catalyzed by mesoporous silicasupported Rh complex and tertiary amine (Scheme 1). The use of mesoporous silica as a support significantly enhances the cooperative catalysis compared with previously reported nonporous silica support system. The effects of pore size on the Rh complex structure and its

Scheme 2. Preparation of (A) MS/diamine/Rh and (B) MS/diamine/Rh/NEt2.

MS/diamine/Rh/NEt₂

Table 2

Elemental analysis results of MS-supported Rh catalysts.

Catalyst	Molar ratio of raw materials ^a [Rh:N(diamine):N(tertiary amine)]	Element (mmol g ⁻¹) ^b		
		С	Ν	Rh
MS(C8)/diamine/Rh	1:2:0	5.8	0.6	0.312
MS(C12)/diamine/Rh	1:2:0	6.9	0.5	0.229
MS(C18)/diamine/Rh	1:2:0	5.3	0.4	0.196
MS(C8)/diamine/Rh/NEt2	1:2:15	21.7	3.1	0.192
MS(C12)/diamine/Rh/NEt ₂	1:2:15	18.5	2.6	0.199
MS(C18)/diamine/Rh/NEt ₂	1:2:15	16.1	2.2	0.143
MS(C18)/diamine/Rh/NEt ₂ (12)	1:2:12	15.9	2.1	0.161
MS(C18)/diamine/Rh/NEt ₂ (7.5)	1:2:7.5	12.6	1.6	0.157

 ^a Charged molar ratio of the diamine/tertiary amine.
 ^b The amounts of C and N were determined by elemental analysis. The amount of Rh was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).



Fig. 1. SEM image of (A) MS(C8)/diamine/Rh and (B) MS(C8)/diamine/Rh/NEt2 and their EDS line analysis results for O, Si, N, and Rh elements.



Fig. 2. Rh K-edge XANES (left) and Fourier Transform of k^3 -weighted Rh K-edge EXAFS spectra (right) of (A) Rh foil, (B) Rh₂O₃, (C) [Rh(cod)OH]₂, (D) MS(C8)/diamine/Rh, (E) MS (C12)/diamine/Rh, (F) MS(C18)/diamine/Rh, (G) MS(C8)/diamine/Rh/NEt₂, (H) MS(C8)/diamine/Rh/NEt₂, (I) MS (C18)/diamine/Rh/NEt₂. The *k* range for FT was k = 3.0-11 Å⁻¹.

Table 3

Curve-fitting analysis for the prepared SiO2-supported Rh catalysts ^a.

Sample	N ^b	R ^c (Å)	$\Delta \sigma^{2 \ d} (\text{\AA} \times 10^{-3})$	ΔE_0 (eV)	Rf (%)
MS(C8)/diamine/Rh MS(C12)/diamine/Rh MS(C18)/diamine/Rh MS(C8)/diamine/Rh/NEt ₂ MS(C12)/diamine/Rh/NEt ₂ MS(C18)/diamine/Rh ^c	$\begin{array}{l} 6.7(\pm 1.1) \\ 6.6(\pm 1.2) \\ 6.5(\pm 1.1) \\ 6.1(\pm 1.0) \\ 6.2(\pm 1.0) \\ 6.5(\pm 1.1) \\ 6.8(\pm 1.5) \end{array}$	$2.09 (\pm 0.01) 2.09 (\pm 0.01) 2.09 (\pm 0.01) 2.09 (\pm 0.01) 2.10 (\pm 0.01) 2.11 (\pm 0.01) 2.09 (\pm 0.02) 2.09 (\pm 0.02) $	$5.81 (\pm 0.29) 7.64 (\pm 0.32) 4.50 (\pm 0.29) 1.02 (\pm 0.36) 1.80 (\pm 0.32) 2.30 (\pm 0.32) 5.35 (\pm 1.68) $	$-4.1(\pm 2.3) -5.3(\pm 2.6) -3.6(\pm 2.4) -0.9(\pm 2.6) -0.8(\pm 2.6) -1.1(\pm 2.4) -10.2(\pm 4.1)$	0.799 1.048 0.792 0.928 0.934 0.895 0.022
SiO ₂ /diamine/Rh/NEt ₂ ^e	6.8(± 1.5)	$2.10 (\pm 0.02)$	5.44 (± 1.75)	$-8.5(\pm 2.3)$	0.022

^a The fitting range of the R-space was 1.0–2.0 (Å). The k range for Fourier Transformation was k = 3-13 (Å⁻¹). Shell: Rh-C/O.

^b Coordination number.

^c Bond distance.

^d Debye-Waller factor.

^e Nonporous SiO₂-supported Rh samples. Data from ref [10a].

catalytic activity are also evaluated.

2. Results and discussion

2.1. Preparation and characterization of catalysts

The mesoporous silica (MS) support used in this study was synthesized according to a well-known sol-gel procedure using primary amines as template molecules [11]. Physicochemical properties of the synthesized MS supports are summarized in Table 1 and are denoted MS (C8), MS(C12), and MS(C18) with 1.6, 2.3, 3.1 Å pore sizes respectively, according to their carbon chain lengths of the template.

The immobilization process of Rh complex and tertiary amine on MS support is shown in Scheme 2. The MS-supported Rh catalysts were prepared according to a similar procedure we reported the preparation of a nonporous silica support [10]. Silane-coupling of 3-(2-aminoethy-lamino)propyltrimethoxysilane with the silica surface afforded MS with

diamine ligand (MS/diamine). A solution of [Rh(cod)OH]₂ in dioxane was added to MS/diamine to afford MS-supported diaminorhodium complex (MS/diamine/Rh). The Rh and tertiary amine immobilized catalyst MS/diamine/Rh/NEt₂, was prepared by attaching 3-(2-aminoethylamino)propyltrimethoxysilane and 3-diethylaminopropyl-trimethoxysilane simultaneously onto the MS surface in 1:15 to 1:7.5 M ratios, followed by complexation with [Rh(cod)OH]₂.

The elemental analysis of prepared MS/diamine/Rh and MS/diamine/Rh/NEt₂ is summarized in Table 2. The carbon and nitrogen amounts for MS/diamine/Rh with different pore diameters, are 5.3–6.9 and 0.4-0.6 mmol/g respectively. The Rh content of 0.2-0.3 mmol/g for MS/diamine/Rh indicates a N/Rh ratio of around 2, suggesting the formation of a diaminorhodium complex. In comparison, the elemental analysis of MS/diamine/Rh/NEt₂ reveals a larger amount of nitrogen and carbon compared to Rh, which clearly indicates the presence of an excess amount of tertiary amine with respect to Rh in MS/diamine/Rh/NEt₂. Samples of MS/diamine/Rh/NEt₂ containing lower amounts of



Fig. 3. *k*³-weighted EXAFS spectra of (A) MS (C18)/diamine/Rh/NEt₂ (solid line) and MS (C18)/diamine/Rh (dashed line), (B) MS(C18)/diamine/Rh (black), MS(C12)/diamine/Rh (blue), MS(C8)/diamine/Rh (red), and (C) MS (C18)/diamine/Rh/NEt₂ (black), MS(C12)/diamine/Rh/NEt₂ (blue), MS(C8)/diamine/Rh/NEt₂ (cred) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 4

Effect of co-immobilized tertiary amine on 1,4-addition reaction ^a.

OH 2.0 mL, 60°C 1 (1.0 mmol) 2 (1.5 mmol) 60 min	
Entry Catalyst Yield (%) ^b	TON
1 $MS(C18)/diamine/Rh/NEt_2$ 65	430
2 MS(C18)/diamine/Rh 33	220
3 MS(C18)/diamine/Rh + triethylamine ^c 50	330
4 MS(C18)/diamine/Rh + diisopropylethylamine ^d 66	440
5 $MS(C18)/diamine/Rh/NEt_2(12)$ 54	360
6 MS(C18)/diamine/Rh/NEt ₂ (7.5) 29	190

^a Reaction conditions: **1** (1.0 mmol), **2** (1.5 mmol), Rh catalyst (Rh: 1.5 μmol), dioxane/H₂O (2.0 mL, 10/1), 60 °C, 60 min.

^b Determined by ¹H NMR.

^c Triethylamine (23 µmol).

^d Diisopropylethylamine (23 µmol).

tertiary amine were also synthesized. Samples with 1:12 and 1:7.5 ratios of Rh:tertiary amine were designated MS/diamine/Rh/NEt₂(12) and MS/diamine/Rh/NEt₂(7.5), respectively. Elemental analysis of these two samples confirmed the lower carbon and nitrogen contents (Table 2).

Homogeneous dispersion of the Rh complex and amine functionalities inside the mesoporous silica was confirmed by SEM-EDX analysis. MS particles with an average size of approx. $0.5 \,\mu$ m were observed for both MS(C8)/diamine/Rh and MS(C8)/diamine/Rh/NEt₂ in the recorded SEM images and the line analysis of elements, shown in Fig. 1. The EDS line analysis results indicate similar location profiles for Rh and N elements relative to Si and O, the main components of MS support, both in the presence and absence of the tertiary amine. These SEM-EDX analysis data clearly support the homogeneous dispersion of Rh complex and amine functionalities inside the mesopores of MS.

Retention of the immobilized tertiary amine structure was confirmed by FT-IR analysis (Figure S1, Supporting Information). The coordination environment of Rh with the diamine ligand in supported catalysts was analyzed by Rh K-edge XAFS. Fig. 2 shows the XANES and FT-EXAFS spectra for MS/diamine/Rh and MS/diamine/Rh/NEt₂ with three types of MS pore diameters along with reference samples. Shapes of the XANES spectra for MS-supported Rh complexes [(D)-(I)] were similar to that of [Rh(cod)OH]₂ (C) but differ largely from Rh₂O₃ (B) and Rh foil (A). In the FT-EXAFS spectra, a strong signal at 1.6 Å assigned as the Rh-O/C/N bond was observed in supported Rh complexes [(D)-(I)]. This signal fits well with the Rh-C/O parameter. The result of

Table 5

Effect of pore size of MS support on 1,4-addition reaction ^a.

1 (1.0 mmo	co + , BroH - H bl) 2 (1.5 mmol)	Rh catalyst (Rh: 1.5 μmol) dioxane/H₂O 2.0 mL, 60°C 60 min	
Entry	Catalyst	Yield (%) ^b	Initial TOF (min $^{-1}$) ^c
1	MS(C8)/diamine/Rh	81	7.3
2	MS(C12)/diamine/Rh	11	1.2
3	MS(C18)/diamine/Rh	33	3.8
4	MS(C8)/diamine/Rh/ NEt ₂	> 99	49.3
5	MS(C12)/diamine/Rh/ NEt ₂	20	2.6
6	MS(C18)/diamine/Rh/ NEt ₂	65	8.0
7	SiO ₂ /diamine/Rh/NEt ₂ ^d	57	6.4

^a Reaction conditions: 1 (1.0 mmol), 2 (1.5 mmol), Rh catalyst (Rh: 1.5μ mol), dioxane/H₂O (2.0 mL, 10/1), 60 °C, 60 min.

^b Determined by ¹H NMR.

 $^{\rm c}$ Initial TOF (min $^{-1}).$ Calculated from initial reaction rate within 10 min and/or at less than 30% conversion.

^d Nonporous silica (Aerosil300, SiO₂) support was used.

curve-fitting analysis of the EXAFS spectra are summarized in Table 3. For MS/diamine/Rh, the coordination numbers (*N*) and bond distances (*R*) were evaluated to be $6.5 \degree 6.7$ and 2.09 Å, respectively. These values are well in agreement with those reported previously for the nonporous SiO₂-supported Rh complex [10], suggesting the formation of a diaminorhodium complex on MS surface, as shown in Scheme 1(A). The difference of curve-fitting analysis results of MS/diamine/Rh from simply adsorbed Rh complex (SiO₂/Rh) [3h] also implies coordination of diamine ligand to the Rh center. The bond distances (*R*) for MS/diamine/Rh/NEt₂ are almost similar to MS/diamine/Rh (2.09–2.11 Å). However, coordination numbers (*N*) are slightly lower than those of

Table 6

R₂

Substrate scope for MS/diamine/Rh/NEt2-catalyzed 1,4-addition reaction of phenylboronic acids ^a.

MS(C18)/diamine/Rh/NEt₂ Ar

MS/diamine/Rh, especially in MS supports with smaller pores (MS(C8) and MS(C12)). Fig. 3 represents k^3 -weighted EXAFS spectra of MS-supported Rh complexes. As shown in Fig. 3(A) and (B), EXAFS spectra of MS(C18)/diamine/Rh/NEt₂, MS(C18)/diamine/Rh, MS(C12)/diamine/Rh, and MS(C8)/diamine/Rh are almost identical. The results are in good agreement with similar curve-fitting analysis results of these samples. In the case of MS/diamine/Rh/NEt₂ with three types of MS pores, EXAFS spectra of the MS(C12) and MS(C8) show small differences with MS(C18) (Fig. 3(C)). These results imply that coordination environment of a part of Rh complex in small pores, MS(C8) and MS (C12), are slightly changed by co-immobilized tertiary amine, due to the direct coordination of tertiary amine to Rh center and/or the steric bulk of the immobilized functionalities with high density in the confined space.

2.2. Catalysis of 1,4-addition reaction of phenylboronic acid

The 1,4-addition catalysis with the prepared MS supported catalysts was evaluated using the addition of phenylboronic acid to cyclohexenone. Reactions of 1.0 mmol of cyclohexenone (1) and 1.5 mmol of phenylboronic acid (2) were examined using 1.5 µmol of Rh in the synthesized MS(C18)-supported Rh catalysts (Table 4). The MS(C18)/ diamine/Rh (entry 2) afforded 33% yield which increased to 65% with the use of MS(C18)/diamine/Rh/NEt2 (entry 1), indicating the beneficial effect of the tertiary amine co-immobilization on the MS surface. The co-immobilization effect of tertiary amine was investigated using a control experiment: addition of triethylamine to MS(C18)/diamine/Rh system slightly enhanced product yield (entry 2 vs 3), however, the TON value was smaller than that of co-immobilized catalyst (entry 1). Addition of diisopropylethylamine was effective for improvement of product yield to 66% (entry 4). Bulkiness of diisopropylethylamine may prevent the direct interaction between amine and Rh center, indicating that the appropriate spacing between two active functionalities is necessary for effective promotion of 1,4-addtion reaction. Therefore, in the case of MS/diamine/Rh/NEt2, the characteristics of the support

EWG +	ArBH(OH) ₂ dioxane/H ₂ O	1 YEWG		
Entry	Unsaturated compound	Arylboronic acid (Ar-)	Time / h	Yield / %
1	(1)	Ph-	2	93
2	~	4-Cl-Ph-	24	92
3		4-CH ₃ C(O)-Ph-	24	99
4		4-CH ₃ O-Ph-	4	92
5		4-CH ₃ -Ph-	4	72
6	() f°	Ph-	24	90
7	Ph Ph	Ph-	5	94 ^b
8		Ph-	24	83
9	Ph	Ph-	24	35
10	Ph CO ₂ Et	Ph-	6	94
11	Ph	Ph-	24	89 ^c

^a Reaction conditions: Unsaturated compound (1.0 mmol), ArB(OH)₂ (1.5 mmol), MS(C18)/diamine/Rh/NEt₂ (Rh: 4.5 μmol), dioxane/H₂O (2.0 nl), 60 °C.

° 100 °C.

Table 7

High TON 1,4-addition reaction using MS/diamine/Rh/NEt2^a.

+ 1 (x mmol)	С В-ОН - Ы ОН 2 (1.5 equiv.)	MS/diamine/Rh/NEt ₂				
Entry	1 / mmol	Rh /µmol	$T \not \ ^oC$	Time / h	Yield (%) ^b	TON
1	1.0	1.50	60	1	> 99	670
2	1.0	0.29	60	60	71	2500
3	1.0	0.29	100	24	85	3000
4 ^c	3.0	0.29	100	24	51	5300
5 °	3.0	0.29	100	96	82	8500

^a Reaction conditions: 2 (1.5 equiv. to 1), dioxane/H₂O (2.0 mL, 10/1), MS(C18)/diamine/Rh/NEt₂.

^b Determined by ¹H NMR.

^c MS(C8)/diamine/Rh/NEt₂.



Scheme 3. Proposed reaction mechanism of MS/diamine/Rh/NEt2-catalzyed 1,4-addition reaction of arylboronic acid.

structure, such as pore size, should influence the cooperative catalytic activity. Decreasing the amount of the co-immobilized tertiary amine induced a decrease in catalytic activity (entries 5 and 6), pointing out the beneficial effect of higher loading density of the co-immobilized

tertiary amine in accelerating the 1,4-addition reaction.

We next examined in detail, the effect of MS pore size on the 1,4addition reaction (Table 5). Among the supports used, MS(C8) possessing the smallest mesopores showed higher catalytic activity, both with and without co-immobilized tertiary amines (entries 1 and 4), indicating enhancement of the 1,4-addition reaction in confined spaces even in the absence of tertiary amine. After co-immobilization of tertiary amine, the activity increased for all MS supports, with MS(C8)/ diamine/Rh/NEt2 delivering the highest catalytic performance. The activity of nonporous silica-supported catalyst (SiO2/diamine/Rh/ NEt₂) was lower than catalysts with MS(C8) and MS(C18) as a support (entry 7). This could be a result of accumulation of the Rh complex, tertiary amine, and surface silanol group in restricted space, which may enhance the active/adsorption site density in mesopore, resulting the effective accumulation/activation of polar substrate molecules [6]. On the other hand, the catalyst with the larger mesopore, MS(C18)/diamine/Rh/NEt₂, showed higher performance than the catalyst with the smaller mesopore, MS(C12)/diamine/Rh/NEt2 possibly due to lower diffusion barrier in larger-pore materials. The detailed underlying reasons for these conflicting results in the pore size effect are unclear. However, one possible explanation is formation of inhomogeneous, highly active catalytic site formation in MS(C8)/diamine/Rh/NEt₂ by accumulation of active functional groups into restricted spaces.

The scope and limitation of 1,4-addition reaction of phenylboronic acid to unsaturated carbonyl compounds are summarized in Table 6. To exclude the size effect of large substrate molecules, MS(C18)/diamine/Rh/NEt₂ was used as the heterogeneous Rh catalyst. The presence of electron-withdrawing and donating groups at the *para*-position of phenylboronic acid had no adverse impact on the reaction, with formation of the corresponding cyclohexenone 1,4-addition product in good to excellent yields (entries 1–5). Other ketones substrates such as cyclopentenone and chalcone afforded high yields under MS(C18)/diamine/Rh/NEt₂-catalysis (entries 6–8). The unsaturated aldehyde afforded the product in lower yield (entry 9). The reaction system tolerates the presence of unsaturated nitriles as acceptors (entries 10 and 11) without any loss in yield. This catalyst system was not applicable to the reaction with olefins without electron-withdrawing group: no addition product was obtained with 1-octene.

We next studied the optimization of the reaction conditions to achieve high turnover number (TON) in the MS/diamine/Rh/NEt₂catalyzed 1,4-addition reaction system (Table 7). 85% yield of the product was obtained even with 0.29 µmol of Rh in MS(C18)/diamine/ Rh/NEt₂ at 100 °C. The reaction of 3.0 mmol of 1 with 0.29 µmol of Rh in MS(C8)/diamine/Rh/NEt₂ afforded 51% yield of 1,4-addition product with a TON of 5300 after 24 h. After a prolonged reaction time, we were pleased to find an increase in the yield and TON to 82% and 8500, respectively. These high TONs compare exceeding well to literature reports. For example, the TONs [12] for reported heterogeneous Rh catalytic systems are as follows: Rh/NiZn, 3200 (4 h);[9k] Rh/HT, 3500 (6 h);[9i] PS-PEG-diene-Rh, 1073 (63 h);[9p] and Rh/Ag nanoparticles, 2200 (16 h and 6 recycle runs).[9l] Our MS/diamine/Rh/NEt₂ system showed higher TON and comparable turnover frequency (TOF) performances compared with reported heterogeneous Rh catalysts.

2.3. Reaction mechanism

The proposed mechanism of the 1,4-addition of phenylboronic acid on the MS/diamine/Rh/NEt₂ surface is shown in Scheme 3. The reaction stopped completely upon filtration of the MS(C18)/diamine/Rh/ NEt₂ catalyst (Figure S2, Supporting Information), indicating the reaction at the MS surface. Phenylboronic acid is adsorbed on the MS surface, likely at the immobilized tertiary amine site (B), leading to the formation of an activated tetra-coordinated boron species, which undergoes facile transmetalation onto the Rh complex to afford the Rh-Ph species (C to D) [13]. The interaction between phenylboronic acid and tertiary amine on the silica surface was detected by ¹¹B MAS NMR measurements, whereby the tetra-coordinated boron species were observed [10]. Our results (Table 4) indicate the enhanced reactivity by the addition of both triethylamine and diisopropylethylamine. As direct N-B interaction with the sterically bulky diisopropylethylamine is highly unlikely, we propose both the direct and indirect (activation by OH-) pathways (C). The Rh-Ph species on MS surface can easily react with the unsaturated ketone, followed by hydration to form the 1,4-addition product and the regeneration of MS/diamine/Rh/NEt₂ catalyst.

3. Conclusion

MS/diamine/Rh/NEt2 was found to be a highly active catalyst for 1,4-addition reaction of phenylboronic acids to unsaturated ketones. Several studies were undertaken to probe the effect of the solid support on catalytic performance. XAFS analysis revealed the local structure of Rh on the MS surface. In all prepared catalysts, the Rh complexes maintained their structure without aggregation. Detailed CF analysis indicates that the pore size of the support slightly affects the local structure of Rh in the case of MS/diamine/Rh/NEt2, suggesting differences in the interactions between Rh complex and immobilized tertiary amine in each mesopore. The catalytic activity of the immobilized Rh complex improved significantly by co-immobilization of a tertiary amine on the same support surface, delivering a high TON of 8500. The MS/diamine/Rh/NEt2-catalyzed reaction was found compatible with a wide range of substrates. These results affirm the relevance of cooperative catalysis between the two immobilized functionalities such as the metal complex and organic group in confined spaces for highly efficient synthesis of fine chemicals.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.04.016.

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