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Concerted Catalysis in Tight Spaces: Palladium-Catalyzed Allylation Reactions Accelerated by Accumulated Active Sites in Mesoporous Silica

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Abstract: The mesoporous silica surface was modified with a Pdbisphosphine complex and/or a tertiary amine group for concerted acceleration of allylation reactions. Mesoporous silica-supported catalysts with 1.6 nm pore diameter showed a higher performance than nonporous or larger mesoporous silica-supported catalysts due to the accumulation of active sites into a confined space. In case of the reaction using allylic alcohol, the presence of the silanol group on the surface was quite effective: the turnover number (TON) of Pd was nine times more than that of the homogeneous Pd complex.

Concerted catalysis between metal complexes and organic functional groups is a notable strategy to create novel heterogeneous catalysis and a highly efficient molecular transformation technique.^[1] Several research groups reported Pd,^[2-10] Rh,^[11] and Cu complexes ^[12,13] immobilized on solid surfaces with other organic functionalities for efficient transformation of organic molecules. In the case of concerted catalysis with Pd complexes, the allylation of nucleophiles was effectively accelerated by the assistance of the basic amine group: both allylic substrates and nucleophiles were activated by Pd complexes and bases, respectively.^[14,15]

Despite the need for more research on the concerted catalysis on solid surfaces, the effect of the support structure on the catalysis between immobilized metal complexes and organic bases has been scarcely studied. In the case of mesoporous support with an appropriate pore diameter, it can be expected that the two immobilized functional groups effectively approached each other for the synergistic activation of substrate molecules ^[16-19] due to the restricted reaction space. In fact, Jones et al. demonstrated that the cooperative catalysis of amine-silanol for aldol reaction was significantly affected by the size of pore diameter.^[19] In other words, mesoporous materials

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have high potential for the support of accumulated multifunctionalities, such as metal complexes and organic bases, for concerted catalysis.

Another important issue with the Pd-catalyzed allylation reaction is the use of less reactive allylic substrates. Allylic alcohol is one of the most desirable allylating agents because the use of allylic alcohol enables minimizing the waste formation by producing only water as a by-product.^[20,21] To promote the reaction with allylic alcohol, the use of protonic acid as a co-catalyst is highly effective ^[22-28]; allylic alcohol can be activated by the hydrogen bond of its hydroxyl group with several weak and strong protonic acids. These facts motivated us to examine the effect of Si-OH groups formed on silica support on the allylic alcohol activation.

Herein, we would like to demonstrate a novel concept for concerted catalysis on the surface: the accumulation of active sites in a tight mesopore space, as shown in Figure 1. The accumulated functions, Pd complexes, tertiary amines, and silanol groups can activate allylating agents, nucleophiles, and leaving groups of allylic alcohol (OH), respectively, resulting in highly efficient allylation reactions.



Figure 1. Concept of mesoporous silica (MS)-supported catalyst design for the Pd-catalyzed allylation reactions.

The distance from the silicon atom to the Pd center and nitrogen atom for the Pd-bisphosphine complex (PP-Pd) and 3diethylaminopropyltrimethoxysilane are approximately 9.0 and 5.5 Å, respectively (Figure 1). We predicted that mesoporous silica (MS) with pore diameters of ~2 nm was suitable for accumulation of these functional groups for concerted catalysis. Various MS supports with different pore diameters in the range of 1.6-3.1 nm were prepared by using primary amine with C8 to C18 alkyl chain as a structure-directing agent.^[29] These MS supports are denoted as MS(C8) to MS(C18). SBA-16 was also used as a reference material with large-sized pores and threedimensional porous network that enhances diffusion and access of reactant molecules to catalytically active sites.^[30] The physicochemical properties of MS are summarized in Table S1 in Supporting Information (SI). The MS samples exhibited high surface areas (855-1865 m²g⁻¹) and narrow pore size

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Figure 2. (A) SEM image of MS(C8)/NEt₂/PP-Pd and line analysis results for Si, P, and Pd elements, (B) ¹³C CP/MAS NMR spectrum of MS(C12)/NEt₂/PP-Pd, (C) ³¹P NMR spectrum of CDCl₃ solution of PP-Pd and ³¹P MAS NMR spectrum of MS(C12)/NEt₂/PP-Pd, and (D) FT of k^3 -weighted Pd K-edge EXAFS spectrum of MS(C12)/NEt₂/PP-Pd.

distributions (1.6-5.3 nm) (Table S1, Figures S1-S3), with the complete removal of structure-directing agents proven by elemental analysis and $^{13}\mathrm{C}$ CP MAS NMR measurments. Nonporous silica (SiO₂, Aerosil300) was also used as a support material to check the effect of mesoporous structre.

Surface functionalization procedure is shown in Scheme 1. The tertiary amine group was immobilized on the MS internal surface by the simple silane-coupling reaction resulting in MS-supported tertiary amine (MS/NEt₂). A Pd-bisphosphine complex with a triethoxysilyl group (PP-Pd) was prepared in line with our previous method.^[10] The Pd complex was introduced to the MS/NEt₂ surface to form MS-supported tertiary amine and PP-Pd (MS/NEt₂/PP-Pd). MS with only the Pd complex (MS/PP-Pd) was also prepared by a similar process.

Elemental analysis results of the prepared samples are summarized in Table S2 in SI. The Pd loading was around 0.3-0.4 mmol g⁻¹ for MS-supported samples. The amounts of nitrogen and carbon in MS/NEt₂/PP-Pd were much higher than thoes in MS/PP-Pd, suggesting the presence of a tertiary amine group with PP-Pd. The almost identical amounts of CI and Pd indicate the presence of the PP-Pd complex.

Small angle XRD analysis revealed that original mesoporous structure was flluly maintained even after the immobilization of organic functionalities. SEM line analysis results are summarized in Figure 2A. The presence of phosphorus and palladium inside the MS(C8) particle was clearly demonstrated





suggesting the existence of immobilized functionalities in the mesopore. The chemical structures of immobilized tertiary amine and PP-Pd were determined by solid-state NMR and Pd K-edge X-ray absorption fine structure (XAFS) measurements. The attachment of functionalities on the MS surface through silanecoupling reaction was confirmed by ²⁹Si MAS NMR measurement: the decrease in the Q^3 site (-100 ppm; Si(OH)₁(OSi)₃) of MS and the generation of T sites (-60~-70 ppm; SiR(OR')₃) were detected after the immobilization (Figure S6, SI). Figure 2B represents solid-state ¹³C CP/MAS NMR spectrum of MS(C12)/NEt₂/PP-Pd. The maintenance of tertiary amine structure was confirmed by the ¹³C NMR signal positions (1~5). The detailed comparison of homogeneous precursors and immobilized material is shown in Figure S7 in SI. The presence of a phenyl group in the PP-Pd complex was also detected around 120-140 ppm, however, other signals of the PP-Pd complex were not clearly detected due to their low intensity.^[10] To confirm the coordination of the phosphine ligand to the Pd center after immobilization, ³¹P MAS NMR measurement was conducted as shown in Figure 2C. The presence of a sharp signal around 0 ppm strongly indicates the coordination of P atoms to Pd in the complex attached to the MS surface.

Pd K-edge X-ray absorption near-edge structure (XANES) spectra of MS/NEt₂/PP-Pd, MS/PP-Pd, SiO₂/NEt₂/PP-Pd, and reference samples are shown in Figure S9 in SI. The spectra of supported Pd complex were almost identical. Their spectral features were similar to PdCl₂(PPh₃)₂, but completely different from PdO and Pd foil. Figure S10 in SI represents k^3 -weighted extended X-ray absorption fine structure (EXAFS) spectra of supported Pd complexes along with the THF solution of the PP-Pd precursor. Similar EXAFS spectra of these samples indicate that the local structure of the Pd complex is not affected by the immobilization on the support surface or by the presence of tertiary amine. Fourier transform (FT) of the k^3 -weighted EXAFS spectra of MS(C12)/NEt₂/PP-Pd is shown in Figure 2D. A strong peak at 1.8 Å was observed and the comparison of this spectrum with PdCl₂(PPh₃)₂ suggested that the peak could be assigned as Pd-P or Pd-Cl, denoted as Pd-P/Cl, bonds. This strong peak was similarly observed in the case of other supported Pd complexes, such as MS/PP-Pd and SiO₂/NEt₂/PP-Pd, as shown in Figure S11 in SI. Table 1 summarizes the results of the curve-fitting analysis using the Pd-P/Cl parameter ChemCatChem

along with the data of PdCl₂(PPh₃)₂ crystal structure.^[31] The peaks for supported Pd complexes were well fitted, with a coordination number (*N*) of approximately 3 and Pd-P/Cl bond length (*r*) of 2.26 Å. These results clearly indicated that the Pd complex structure was maintained after immobilization on the support. Larger Debye-Waller factor ($\Delta\sigma^2$) value of MS(C12)/NEt₂/PP-Pd compared with MS(C12)/PP-Pd suggests the steric effect of the tertiary amine group on the Pd complex co-immobilized on the same solid surface. From these characterization results of the elemental analysis, NMR, and XAFS, the proposed structure of MS/NEt₂/PP-Pd is shown in Scheme 1.

Table 1. Curve-fitting	analysis of EXAFS	spectra for PP-Pd	complexes. ^[a]
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Sample	Shell	N ^[b]	r ^[c] [Å]	∆σ ^{2 [d]} [Å ² ×10 ⁻³]	∆ <i>E</i> ^[e] [eV]	Rf ^[f] [%]
MS(C12)/NEt_/P		27	2.25	4 86	-8.65	
	Pd-P/Cl	2.7	2.20	+.00	-0.00	0.086
F-FU		±0.4	±0.01	±0.23	±2.12	
		2.9	2.27	2.80	-3.29	0 1 1 2
M3(C12)/PP-Pu	Pu-P/CI	±0.4	±0.01	±0.23	±2.09	0.142
SiO ₂ /NEt ₂ /PP-		3.0	2.26	5.43	-5.14	0.057
Pd	Pa-P/CI	±0.5	±0.01	±0.23	±2.09	0.057
MS(C12)/NEt ₂ /P		2.1	2.26	4.68	-12.8	0.500
P-Pd (used)	Pa-P/CI	±0.3	±0.01	±0.23	±2.22	0.592
PP-Pd	5 . 5 . 6 .	3.0	2.29	2.64	-5.89	
(THF solution) ^[g]	Pd-P/Cl	(fix)	±0.01	±0.03	±1.91	1.28
Pd(II)Cl ₂ (PPh ₃) ₂	(Pd-P)	2	2.34 ^[j]			Č
[1]	(Pd-Cl)	2	2.30 ^[j]			

[a] Fourier transform and Fourier-filtering regions were limited, where $\Delta k = 2.8 \sim 15 \text{ Å}^{-1}$. and $\Delta r = 1.4 \sim 2.2 \text{ Å}$, respectively. [b] Coordination number. [c] Bond distance between absorber and backscatter atoms. [d] The Debye-Waller factor (DW), which is relative to the DW of the reference. [e] The inner potential correction accounts for the difference in the inner potential between the sample and reference. [f] The goodness of curve fit. [g] Homogeneous THF solution of the PP-Pd complex. [i] Data from ref. [21] [j] Average value was reported.

Allylation of ethyl acetoacetate with allylmethylcarbonate was carried out by using Pd complex catalysts. The results are summarized in Table 2. MS(C12)/PP-Pd showed slightly higher activity (TON=190) than SiO₂/PP-Pd (TON=110). Surprisingly, the catalytic performances of MS supported catalysts were significantly enhanced by the co-immobilization of the tertiary amine group on the same support surface: MS(C12)/NEt₂/PP-Pd showed TON value of 460. This value is much higher than that of the nonporous catalyst with both Pd complexes and tertiary amines (SiO₂/NEt₂/PP-Pd: TON=220). The TON value of the tertiary amine-Pd complex catalysts (MS(C8~18)/NEt₂/PP-Pd) with MS support synthesized with primary amine template was more than 460 for the pore diameter range of 1.6-3.1 nm, however, this value suddenly dropped to the value of the nonporous support when the pore size increased to more than 5.3 nm (TON=210).

Table 3 summerized effect of pore size and Pd grafting density on the initial turnober frequency (TOF) of the allylation reaction. Pd grafting density was calculated from Pd loading (μ mol g⁻¹) and the surface area of MS support (m² g⁻¹). To determine the initial TOF of each MS-supported catalyst, the

substrate/catalyst ratio was increased from 256 (Table 2) to 1000 (Table 3). As shown in Table 3, the catalytic activity increased with decreasing pore diameter of the MS support. Moreover, the time course of allylation reactions in Figure S12 also indicate that catalyst performance was enhanced by small pore size. On the other hand, Pd grafting density did not strongly affect catalytic activity. These results suggest that pore curvature is essential for the catalysis,^[19] and that "two dimensional" accumulation of active species cannot strongly improve the catalytic performance. Catalysts with small pores (i.e., high pore curvature) showed higher activity than those with large pores (i.e., low pore curvature), suggesting that "threedimensional" accumulation of active species can effectivly accelerate catalytic reactions.

Table 2. The allylation catalyzed by SiO_2 -supported Pd complexes ^[a]

EtO Me + (2.5 equ	OMe Pd catalyst toluene, K ₂ CC iv.) 70 °C, 60 min		Me	
Catalyst	Pore size of MS	Conv	Yield	TON
	support [nm] ^[b]	. [%]	(mono/di)	[Pd ⁻¹]
			[%]	[c]
SiO ₂ /PP-Pd	-	38	35 / 3	110
MS(C12)/PP-Pd	2.3	62	49 / 12	190
SiO ₂ /NEt ₂ /PP-Pd	-	68	51 / 17	220
MS(C8)/NEt ₂ /PP-Pd	1.6	98	6 / 93	490
MS(C10)/NEt ₂ /PP-Pd	1.9	99	17 / 83	470
MS(C12)/NEt ₂ /PP-Pd	2.3	99	18 / 80	460
MS(C18)/NEt ₂ /PP-Pd	3.1	98	11 / 86	470
SBA-16/NEt ₂ /PP-Pd	5.3	72	54 / 14	210

[a] Reaction conditions: ethyl acetoacetate (1.0 mmol), allylmethylcarbonate (2.5 equiv. to ketoester), Pd catalyst (Pd: 3.9 µmol), K_2CO_3 (0.50 mmol), toluene (2 mL), 70 °C, 60 min. [b] Determined by BJH method. [c] TON was calculated as follows: TON = (moles of nucleophile)×[(yield of the mono-product) + 2×(yield of the di-product)] / (moles of Pd).

Table 3. Effect of pore size and Pd grafting density on the initial TOF of the allylation reaction

anylation reaction			
Catalyst	Pore size of MS	Pd grafting	Initial
	support [nm] ^[a]	density	TOF [Pd ⁻¹
		[µmol m ⁻²] ^[b]	h ⁻¹] ^[c]
MS(C8)/NEt ₂ /PP-Pd	1.6	0.15	1240
MS(C12)/NEt ₂ /PP-Pd	2.3	0.33	890
MS(C18)/NEt ₂ /PP-Pd	3.1	0.22	610
SBA-16/NEt ₂ /PP-Pd	5.3	0.33	240
SiO ₂ /NEt ₂ /PP-Pd	-	0.57	220 ^[d]

[a] Determined by BJH method. [b] Calculated as follows: (Pd grafting density) = (Pd loading [µmol g⁻¹])/(Surface area [m² g⁻¹]). [c] Reaction conditions: ethyl acetoacetate (1.0 mmol), allylmethylcarbonate (2.5 mmol), MS/NEt₂/PP-Pd (Pd: 1.0 µmol), K₂CO₃ (0.17 mmol), toluene (4 mL), 70 °C. The initial TOF was calculated from the TON value at 1 h. [d] Reaction conditions of Table 2.

The Pd-catalyzed allylation is usually started by the reaction between a Pd(0) species and an allylating agent to form π allylpalladium which undergoes addition of a nucleophile. In our case, in-situ formation of Pd(0) complex by the removal of chlorine from the PP-Pd(η^1 -allyl)Cl complex by the reaction with ethyl acetoacetate was proposed (Scheme S1 in SI).^[10] After the

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allylation, the solid catalyst MS(C12)/NEt₂/PP-Pd was recovered and the XAFS measurement was conducted. As shown in Table 1, *N* value decreased to 2.1 in the used MS(C12)/NEt₂/PP-Pd. This result supports (i) the activation process, removal of chlorine from Pd center, as mentioned above and (ii) easy access of substrate molecules to almost all of the Pd complexes located inside the mesopore. After the formation of active Pd(0) species, successive reactions with the allylating agent formed π allylpalladium (Figure 3A). During the catalytic cycle, the tertiary amine group, which is close to the Pd complex, simultaneously activates the nucleophile to accelerate the allylation reaction (Figure 3A).



Figure 3. (A) Basic and (B) acidic acceleration of the allylation reaction using allylmethylcarbonate and allyl alcohol, respectively.

To examine the stability of the catalyst, the substrate/catalyst ratio was increased. The reaction of 15 mmol of the ketoester smoothly proceeded in the presence of 0.5 µmol of Pd in MS(C8)/NEt₂/PP-Pd with a TON value of up to 22,700 (Scheme 2A). A phenol derivative can also be used as a nucleophile. The reaction between bisphenol A and allyl acetate resulted in a 98% yield of double allylated product for 4 h with a total TON of 1,960 2B). The product, 4,4'-(propane-2,2-(Scheme divl)bis(allyloxybenzene), is a potentially useful precursor of bisglycidyl ether, a monomer of epoxy resin.^[32,33] therefore. the allylation of bisphenol A without allyl halide is a highly desirable chemical process. The product yield and TON of our catalyst system are much higher than those of the previously reported non-halogenated systems for double allylation of bisphenol A, such as [RuCp(PPh₃)₂]⁺: yield=51%, TON=260;^[33] Pd(OAc)₂: 24%, 240;^[33] Pd₂(dba)₃: 98%, 80;^[34] Pd/Carbon: 65.8%, 1300,^[35] or comparable with the homogeneous Pd(OAc)₂ system reported in a patent (TON=3000).[32

Next, the reaction using allylic alcohol instead of carbonate and acetate was examined using the MS-supported Pd catalyst. In this case, the catalyst with tertiary amine did not show activity, whereas, MS with only Pd complex (MS(C12)/PP-Pd) acted as a good catalyst (TON=87), as shown in Figure 4. Calcination of MS(C12) support at 540 °C (MS(C12,cal)) before attachment of PP-Pd induced decreasing activity (TON=68). The TON value also decreased by the treatment of the surface Si-OH group by (MeO)₃SiMe before catalytic reaction (TON=31). These results indicate the participation of the Si-OH group in the catalytic reaction. Despite the similar density of surface Si-OH (Table S1 in SI), nonporous SiO₂ was not good support for the reaction (TON=24), indicating that mesoporous structure is effective for the concerted activation of allylic alcohol. Interestingly, the immobilization of PP-Pd on the MS support enhanced its performance nine times the value of homogeneous PP-Pd (TON=10). The MS(C12)/PP-Pd-catalyzed allylation with allylic alcohol successfully proceeded with only 0.1 mol% of Pd: the TON value of MS(C12)/PP-Pd was up to 820 under solvent free conditions (Scheme 2C). In the case of the reaction with allylic alcohol, the MS(C8)/PP-Pd catalyst with small pores showed performance similar to that of the MS(C12)/PP-Pd. The effect of pore size on the above reaction with allylic alcohol is currently investigated.



Scheme 2. High TON allylation with (A) allylmethylcarbonate, (B) allyl acetate, and (C) allylic alcohol.





 $^{\circ}C,$ 60 min. A small amount of di-substituted product was formed (Table S3) [a] Si-OH group was treated with (MeO)_3SiMe.

In order to determine the interaction between allylic alcohol and MS surface, ^{13}C CP/MAS NMR measurement of allylic alcohol adsorbed on MS was conducted. As shown in Figure 5, new broad signals (C1' and C3') could be observed. In the case of allylic alcohol adsorbed on H-ZSM-5, the C1' signal shifted from 64 to 71 ppm ($\Delta \overline{\texttt{D}}\texttt{=4}$ ppm).^{[36]} The C1' signal on MS also showed a downfield shift with a smaller $\Delta \overline{\texttt{D}}$ value (1.5 ppm) suggesting a weak acidic interaction between the hydroxyl group of allylic alcohol and Si-OH to accelerate the $\pi\text{-allylpalladium}$ formation (Figure 3B).

In summary, this study demonstrated the concerted catalysis between the Pd complex and tertiary amine/silanol in mesoporous silica. The reactions using allylmethylcarbonate/allylacetate were effectively accelerated by tertiary amine immobilized into the same mesopore with the Pd complex. The catalytic activity strongly depended on the pore diameter: a tight space was more effective than a relatively large pore. Allylic alcohol, a tough allylating agent, was activated by a Si-OH group on the MS surface, resulting in a higher catalytic performance of MS/PP-Pd compared with the homogeneous Pd complex. The precise control of the support morphology is a high-potential approach for the enhancement of the concerted catalysis on the surface.



Figure 5. ¹³C CP/MAS NMR spectrum for allylic alcohol adsorbed on MS surface.

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Concerted catalysis between the Pd complex and tertiary amine/silanol in mesoporous silica enables highly efficient allylation of nucleophiles with allyl methyl carbonate, allyl acetate, and also allylic alcohol.



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