

# Concerted Catalysis by Pd Complex on Mesoporous Silica for Allylation Reactions with Allylic Alcohol

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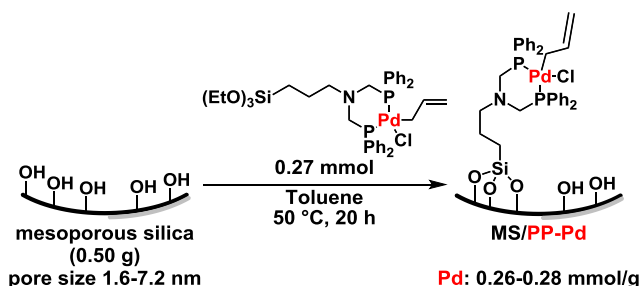
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The use of allylic alcohol, a less reactive allylic substrate, is an ideal approach in allylation reaction of nucleophiles (Nu-H) because the by-product is only water. To promote the reaction with allylic alcohol, the use of protonic acid as a co-catalyst is highly effective[1]; allylic alcohol can be activated by the hydrogen bond of its hydroxyl group with several weak and strong protonic acids. Herein, we would like to present the effect of (i) Si-OH groups formed on silica support and (ii) mesoporous structure of catalyst support on the allylic alcohol activation.

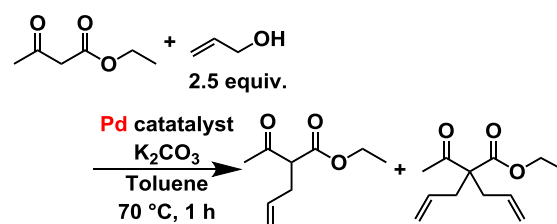
Mesoporous silica (MS) with pore diameter of 2.3 nm was synthesized using a primary amine as a structure-directing agent. As shown in Scheme 1, a Pd-bisphosphine complex with a triethoxysilyl group (PP-Pd) was immobilized on the MS internal surface by the simple silane-coupling reaction resulting in MS-supported PP-Pd (MS/PP-Pd). The structure of MS/PP-Pd was characterized by XRD, SEM, XPS, solid-state NMR and Pd K-edge XAFS.

The results of allylation of ethyl 3-oxobutanoate with allylic alcohol using Pd catalysts are summarized in Table 1. MS with only Pd complex (MS/PP-Pd) acted as a good catalyst (TON=87). Calcination of MS support at 540 °C for 3 h before attachment of PP-Pd (MS(cal)/PP-Pd) induced decreasing activity (TON=68). Similarly, the TON value also decreased with MS/PP-Pd-cap, which was treated with (MeO)<sub>3</sub>SiMe to remove the surface Si-OH group (TON=31). Moreover, nonporous silica (SiO<sub>2</sub>) was not good support



**Scheme 1.** Preparation of MS/PP-Pd

**Table 1.** Allylation with allylic alcohol catalyzed by Pd complexes



Pd cat	Si-OH [mmol/g]	yield (mono/di) [%]	TON
MS/PP-Pd	4.1	47/3	87
MS(cal)/PP-Pd <sup>[a]</sup>	3.3	38/1	68
MS/PP-Pd-cap <sup>[b]</sup>	—	19/0	31
SiO <sub>2</sub> /PP-Pd	3.5	14/0	24
PP-Pd	—	6/0	10

[a] Mesoporous silica was calcined (540 °C, 3 h).

[b] MS/PP-Pd was treated with trimethoxy(methyl)silane (0.18 mmol) in toluene (1.0 mL) for 40 °C, 1 h.

for the reaction (TON=24). In the reaction using homogeneous Pd catalyst, the activity was quite decreased. These results indicate that both Si-OH group and mesoporous structure are effective for activation of allylic alcohol. An interaction between MS surface and allylic alcohol adsorbed on the MS was revealed by <sup>13</sup>C CP/MAS NMR measurement. Hydrogen bonding between hydroxyl group of allylic alcohol and surface Si-OH may enhance the formation of a  $\pi$ -allylpalladium intermediate.

## REFERENCES

- [1] K. Manabe, S. Kobayashi, *Org. Lett.*, 5 (2003) 3241; F. Ozawa, H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami, M. Yoshifuji, *J. Am. Chem. Soc.*, 124 (2002) 10968; H. Kinoshita, H. Shinokubo, K. Oshima, *Org. Lett.*, 6 (2004) 4085; I. Usui, S. Schmidt, M. Keller, B. Breit, *Org. Lett.*, 10 (2008) 1207; I. Usui, S. Schmidt, M. Keller, B. Breit, *Org. Lett.*, 11 (2009) 1453.