

Concerted Catalysis of Pd Complex on Mesoporous Silica Surface for Acceleration of Allylation of Nucleophiles

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Abstract: Various mesoporous silica (MS) with different pore diameters in the range of 1.6-3.1 nm were prepared. The tertiary amine group was immobilized on the MS internal surface by the simple silane-coupling reaction, then Pd complex (PP-Pd) was introduced to the surface to form MS-supported tertiary amine and PP-Pd (MS/NEt₂/PP-Pd). MS supported only PP-Pd (MS/PP-Pd) was also prepared by similar procedure. The prepared catalysts were characterized by spectroscopic techniques including XAFS. The prepared supported catalysts showed high catalytic performance due to concerted effect between Pd complex and tertiary amine/surface silanol for allylation of nucleophiles using various allylating agents including allylic alcohols.

Keywords: Concerted catalysis, Pd complex, allylation.

1. Introduction

Concerted catalysis between metal complexes and organic functional groups is a notable strategy to accelerate catalytic reactions.¹ Our group already reported nonporous SiO₂-supported Pd bisphosphine complex and tertiary amine for the efficient allylation of nucleophile.² Allylic substrates and nucleophiles are activated by Pd complexes and bases, respectively.

Despite the need for more research on the concerted catalysis on solid surfaces, the effect of the support structure on the allylation between immobilized Pd complexes and tertiary amine 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 (Figure 1A).

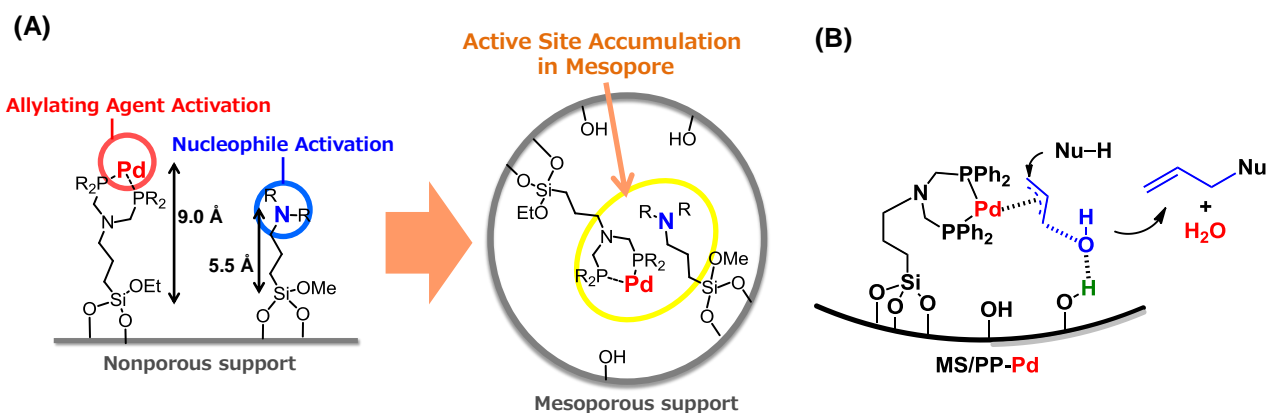


Figure 1. (A) Concept for active site accumulation in mesopore and (B) allylic alcohol activation by surface silanol.

Another important topic for the allylation is use of allylic alcohol as an allylating agent. 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; allylic alcohol can be activated by the hydrogen bond of its hydroxyl group with several weak and strong protonic acids. These facts encouraged us to examine the effect of Si-OH groups on mesoporous silica (MS) surface for the activation of allylic alcohol, as shown in Figure 1B.

Herein, we would like to demonstrate concerted catalysis between a Pd complex and tertiary amine in MS.³ Additionally, effect of surface silanol for the allylation using allylic alcohol will also be presented.³

2. Experimental

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. SBA-16 was also used as a reference material with large-sized pores (5.3 nm). The tertiary amine group was immobilized on the MS internal surface by the simple silane-coupling reaction, then Pd complex (PP-Pd) was introduced to the surface to form MS-supported tertiary amine and PP-Pd (MS/NET₂/PP-Pd). MS supported only PP-Pd (MS/PP-Pd) was also prepared similar procedure. The structure of catalyst was characterized by XRD, SEM, XPS, solid-state NMR and Pd K-edge XAFS. These spectroscopic analysis results clearly indicate the maintenance of the PP-Pd complex structure after the immobilization on MS surface.

3. Results and discussion

The allylation of ethyl 3-oxobutanate with allylmethylcarbonate using MS/NET₂/PP-Pd was conducted. The catalyst with 1.6 nm mesopore showed the highest activity for the allylation (TON=1590, 3 h). The catalytic activity slightly decreased with increasing pore diameter to 3.1 nm (TON=1400). SBA-16 with larger pore size did not show good catalytic performance (TON=475). These results clearly indicate that the small pore diameter induces high catalytic performance. Possible reaction pathway is as follows: proton abstraction from a nucleophile by the tertiary amine close to the Pd complex accelerates the nucleophilic addition step.

MS/PP-Pd acted as a good catalyst for allylation of ethyl 3-oxobutanate with allylic alcohol (TON=87, 3 h). Calcination of MS support at 540 °C for 3 h before attachment of PP-Pd induced decreasing activity (TON=68). Similarly, the TON value also decreased with MS/PP-Pd treated with (MeO)₃SiMe to remove the surface Si-OH group (TON=31). In the reaction using homogeneous Pd catalyst, the activity was quite decreased (TON=10). These results indicate that Si-OH group is effective for activation of allylic alcohol. An interaction between MS surface and allylic alcohol adsorbed on the MS was revealed by spectroscopic analysis.

4. Conclusions

Concerted catalysis between Pd complex and tertiary amine on same solid surface was significantly enhanced by the mesoporous structure of their support. Especially, the mesoporous silica with 1.6 nm pore diameter showed the highest performance compared with other mesoporous silica with larger pore or nonporous silica support. The MS/PP-Pd was also found to be a good catalyst for allylation reaction with allylic alcohol. The results indicate that the surface Si-OH group and mesoporous structure are effective for activation of allylic alcohol. The accumulated active species, Pd complex/tertiary amine/silanol group, in mesopore, effectively accelerate allylation of nucleophile.

References

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