

# Concerted Catalysis in Mesoporous Silica: Palladium-Catalyzed Allylation Accelerated by co-Immobilized Tertiary Amine

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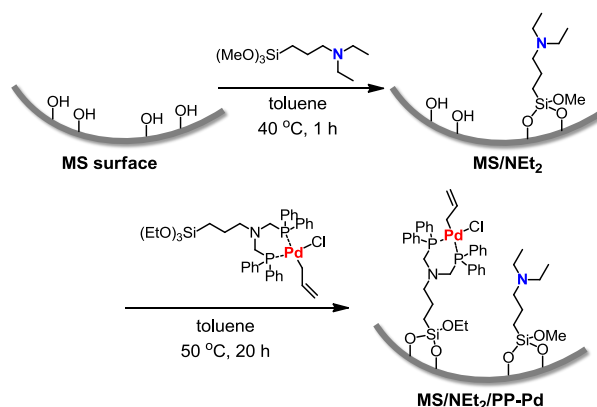
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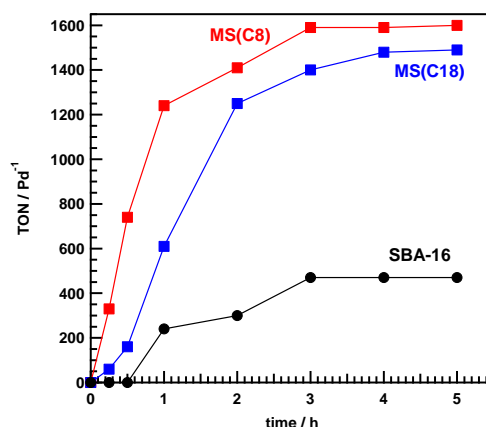
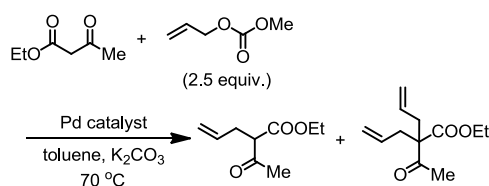
Concerted catalysis between metal complexes and organic functional groups is a notable strategy to accelerate catalytic reactions.[1] Our group already reported nonporous SiO<sub>2</sub>-supported Pd bisphosphine complex and tertiary amine for the efficient allylation of nucleophile.[2] Allylic substrates 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. Herein, we would like to demonstrate concerted catalysis between a Pd complex and tertiary amine in mesoporous silica (MS).

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/NEt<sub>2</sub>/PP-Pd) (Scheme 1). The prepared catalysts were characterized by XRD, SEM,



**Scheme 1.** Preparation of MS/NEt<sub>2</sub>/PP-Pd



**Fig. 1** Allylation using MS/NEt<sub>2</sub>/PP-Pd with various pore sizes.

XPS, solid-state NMR, and Pd K-edge EXAFS

Fig. 1 shows the time course for the allylation using MS/NEt<sub>2</sub>/PP-Pd with various pore sizes. These results clearly indicate that the small pore diameter induces high catalytic performance. Detailed reaction mechanisms will be discussed in presentation.

## REFERENCES

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