

Al-doped Mesoporous Silica-supported Pd Complex Catalyst for the Tsuji-Trost Allylation

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Allylation using allylic alcohol is friendly to the environment because the water is the only byproduct. Allylic alcohol is one of the most unreactive allylating agents in the most homogeneous Pd-catalyzed allylation reaction systems.[1,2] Heterogeneous catalysts are known for their unique catalytic performance caused by the concerted catalysis effect with both immobilized metal center and supporting material surface. Our laboratory has developed a mesoporous silica supported Pd complex catalyst recently, which promotes the Tsuji-Trost type allylation of dicarbonyl and cyanide compounds using allylic alcohol and its derivatives.[3] The catalyst promotes the reaction by activating the unactivated allylic alcohol through the establish of hydrogen bonds between allylic alcohol and surficial silanol groups. Otherwise, the doping of alumina into silica would increase the acidity on the surface, by the electron withdrawing effect and its unoccupied orbitals.

In this work, a series of aluminium doped mesoporous silica (MS-Al) supported Pd complexes with diphenyl phosphine ligand (Figure 1) were synthesized and characterized through NMR, FT-IR, ICP and XAFS. FT-IR pyridine adsorption experiment found bare Brønsted acid sites but abundant Lewis acid sites after immobilization, which may activate the allylic alcohol in the reaction acceleration. In the case of allylic alcohol scope, we found that modifying the surface acidity by the addition of Al can affect their reactivity. Other supports like pure mesoporous silica (MS/PP-Pd) and calcinated mesoporous silica (MS(cal)/PP-Pd) were also examined. The catalytic performance for simple allylic alcohol was increased by Al-doping, while the reactivity enhanced further in the case of allylic alcohols with substitution groups. Acidic activation of the substituted allylic alcohols by Al site may promote the C-O bond cleavage. On the other hand, the MS(cal) support showed the low activity due to the decreased Si-OH group on its surface.

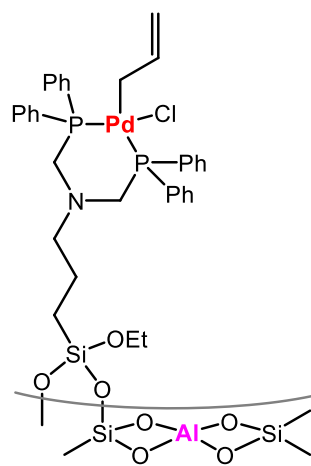


Figure 1. Structure of MS-Al/PP-Pd

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