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Title(English)	Heterogeneous Concerted Catalysis by Metal Complex and Organic Base Immobilized on Same Solid Surface
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The present dissertation deals with studies on concerted catalysis by metal complexes and organic bases on a silica surface. To realize such a concept, catalysts were prepared via functionalization of a silica surface with a diamine ligand and tertiary amine (SiO_2/diamine/NEt_2) followed by complexation with metal species. The outline of this study are as follows: [Chapter II] synergistic catalysis by a palladium complex and tertiary amine on a silica surface, [Chapter III] double-activation catalysis by a rhodium complex and tertiary amine on a silica surface, and [Chapter IV] direct estimation of the distance between immobilized functional groups for concerted catalysis using a probe molecule.

In chapter II, I report the synergistic catalysis of the Tsuji-Trost allylation by a silica-supported diaminopalladium complex and a tertiary amine (SiO_2/diamine/Pd/NEt_2). The structures of the prepared catalysts were investigated by ^{29}Si MAS and ^{13}C CP/MAS NMR, XPS, and elemental analysis. The palladium-catalyzed reaction was significantly accelerated by the assistance of the tertiary amine. The reaction mechanism using SiO_2/diamine/Pd/NEt_2 involves activation of the allylating reagent by the Pd complex and nucleophile by the tertiary amine, which were clarified by ^{13}C CP/MAS NMR measurement. The SiO_2/diamine/Pd/NEt_2 catalyst exhibited wide applicability and high selectivity in the reaction using various substrates such as 1,3-dicarbonyls, phenols, and carboxylic acids. Moreover, the catalyst was reusable at least four times without appreciable loss of its activity and selectivity.

In chapter III, I describe the double-activation catalysis of the 1,4-addition of organoboronic acids to an α,β-unsaturated carbonyl compound by a rhodium

complex/tertiary amine catalyst (SiO_2/diamine/Rh/NEt_2). The catalysts were characterized by ^{29}Si MAS and ^{13}C CP/MAS NMR, X-ray absorption fine structure (XAFS), XPS and elemental analysis. The immobilized tertiary amine successfully accelerated the Rh-catalyzed 1,4-addition. The acceleration mechanism of the reaction was clarified by ^{11}B MQ MAS NMR measurement. The surface tertiary amine reacted with the boron species to form a four-coordinate boron species, which led to the acceleration of the rate-determining trasmetalation step. The catalyst system could be applied to the reactions of various aryl- and alkyl-boronic acids.

In chapter IV, I describe the estimation of the distance between immobilized functional groups for concerted catalysis using a probe molecule. In chapters II and III, SiO_2/diamine/Pd/NEt_2 and SiO_2/diamine/Rh/NEt_2 catalysts were synthesized from a platform material possessing a diamine ligand and a tertiary amine base on the same silica surface (SiO_2/diamine/NEt_2). At the immobilization process of the diamine ligand and tertiary amine, the distance between active sites was determined in such concerted catalysis. Therefore, the distance between the diamine ligand and tertiary amine was investigated in this chapter. The distance between active sites is discussed based on the interaction between the functionalized SiO_2 surface and a probe molecule, *p*-formyl phenylboronic acid. The interaction was studied by ^{11}B MAS and ^{13}C CP/MAS NMR and FT-IR measurement.