

論文 / 著書情報
Article / Book Information

題目(和文)	同一固体表面に固定した金属錯体と有機塩基による協同触媒作用
Title(English)	Heterogeneous Concerted Catalysis by Metal Complex and Organic Base Immobilized on Same Solid Surface
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第10214号, 授与年月日:2016年3月26日, 学位の種別:課程博士, 審査員:本倉 健,稲田 宗隆,小坂田 耕太郎,馬場 俊秀,穴戸 厚
Citation(English)	Degree:, Conferring organization: Tokyo Institute of Technology, Report number:甲第10214号, Conferred date:2016/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

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 ($\text{SiO}_2/\text{diamine}/\text{NEt}_2$) 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 ($\text{SiO}_2/\text{diamine}/\text{Pd}/\text{NEt}_2$). 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 $\text{SiO}_2/\text{diamine}/\text{Pd}/\text{NEt}_2$ 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 $\text{SiO}_2/\text{diamine}/\text{Pd}/\text{NEt}_2$ 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 ($\text{SiO}_2/\text{diamine}/\text{Rh}/\text{NEt}_2$). 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 transmetalation 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, $\text{SiO}_2/\text{diamine}/\text{Pd}/\text{NEt}_2$ and $\text{SiO}_2/\text{diamine}/\text{Rh}/\text{NEt}_2$ catalysts were synthesized from a platform material possessing a diamine ligand and a tertiary amine base on the same silica surface ($\text{SiO}_2/\text{diamine}/\text{NEt}_2$). 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.