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種別(和文)	要約
Type(English)	Outline

Surface Design of Silica-Supported Metal Complex for Enhanced Catalysis

Kyogo Maeda

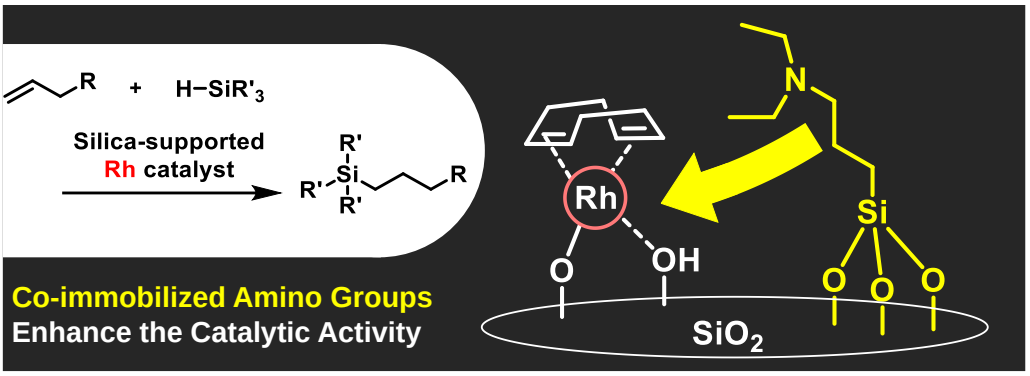
Abstract

Generally, the catalytic activity, stability, and selectivity of immobilized metal complexes is strongly affected by many structural factors such as the length of the anchor between the metal center and the surface, the presence of co-immobilized functionalities on the same surface, and inorganic functional groups originating from the support. Additionally, the performance of supported catalysts usually reflects the effect of substrate functional groups, e.g., the electron-donating and -withdrawing groups on aromatic rings. Thus, a deep understanding of these factors aids the development of high-performance supported catalysts.

The environment of a surface-attached catalytic metal center is completely different from that of a metal center in a homogeneous catalyst. At the single-molecule scale, in other words, for the first coordination sphere, the structure–catalytic activity relationship is difficult to understand. However, this is the conventional concept for understanding homogeneous catalysis. To understand supported catalysis in detail, one should account for the surroundings of the second coordination sphere using precise and long-range characterization as well as target-focused control experiments.

The present study deals with the relationship between catalyst surface design (including that of the outside of the first coordination sphere) and catalytic activity, aiming to develop highly active catalysts featuring metal complexes immobilized on silica supports. The catalysts are prepared by simple silane coupling and analyzed by advanced spectroscopic techniques such as solid-state NMR, in situ FT-IR, and low-temperature XAFS measurements. The main topics are shown in **Figure 1**

[Chapter II]



[Chapter III]

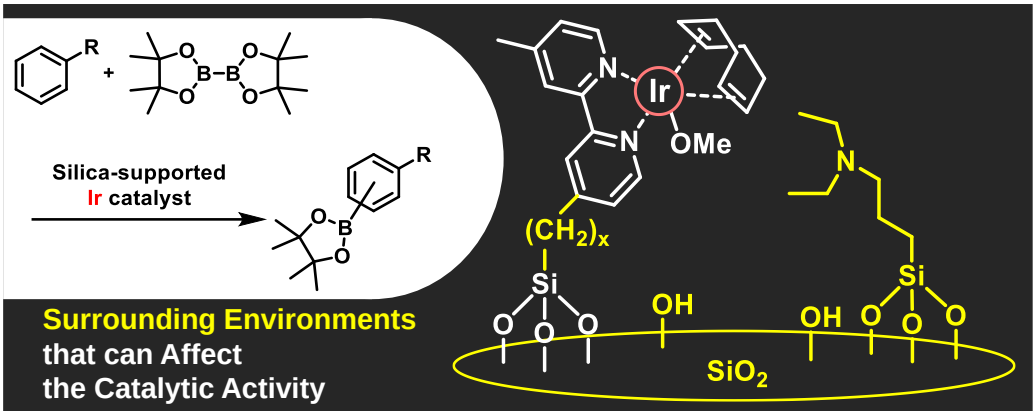


Figure 1 Outline for this study

Chapter II deals with the improvement of catalytic activity by structural control of the outside of the first coordination sphere using co-immobilized organic functional groups. Silica-grafted Rh complex catalysts are prepared for hydrosilylation, and their structures are investigated by elemental analysis, ^{29}Si MAS NMR, ^{13}C NMR, FT-IR, and XAFS measurements. The catalyst with a Rh complex and a tertiary amine supported by SiO_2 (SiO_2/Rh-NEt_2) is revealed to show higher activity than the catalyst where only the Rh complex is immobilized (SiO_2/Rh), featuring a TON of 1 900 000 and a wide substrate scope.

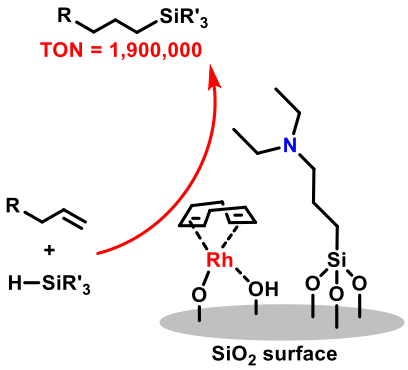


Figure 2 SiO_2/Rh-NEt_2 catalyst for efficient hydrosilylation reaction

Chapter III focuses on co-immobilized functional groups as well as the linker length and functional groups on the silica surface (Si–OH), reporting aromatic C–H borylation catalyzed by a SiO_2-immobilized Ir complex catalyst. The structures of the prepared catalysts are characterized by elemental analysis, ^{13}C NMR, FT-IR, and XAFS measurements. When benzonitrile (Ph–CN) is used as a substrate, catalytic activity is shown to be significantly affected by the co-immobilized organic functionality and the linker length of the Ir-bipyridine complex, increasing by one order of magnitude when the distance between the Ir complex and the silica surface is decreased. The type of substituents on the aromatic substrate is demonstrated to affect the trend of the appropriate catalyst structure. Moreover, the co-immobilization of a tertiary amine is demonstrated to enhance catalytic activity. The above properties are elucidated by in situ FT-IR, Raman, and XAFS measurements.

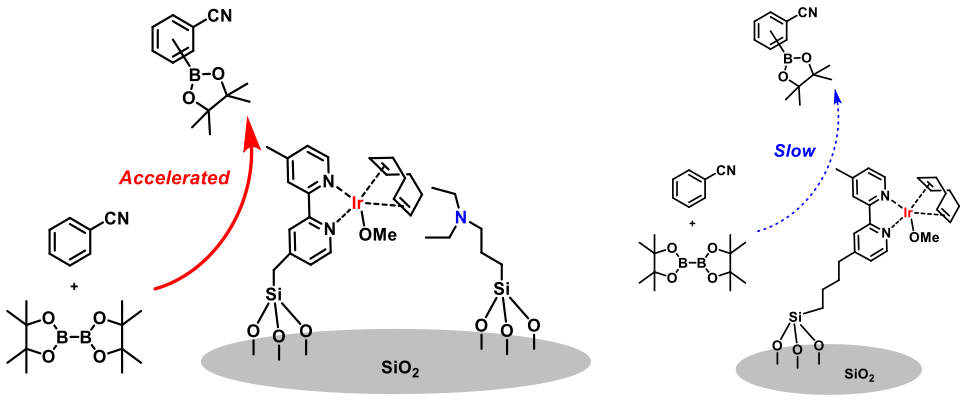


Figure 3 SiO_2/ NEt_2/bpy(C_1)/Ir catalyst for efficient hydrosilylation reaction