

Concerted Catalysis by Immobilized Rh Complex and Tertiary Amine on SiO₂ Surface for Hydrosilylation of Olefins

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The hydrosilylation reaction is widely used for the synthesis of organosilicon compounds which are industrially useful intermediates and products. It has been reported that a catalyst, SiO₂/Rh, in which the Rh complex is immobilized on the surface of silica, shows high activity for hydrosilylation reaction.[1] On the other hand, our group has reported the catalyst with both a Rh complex and tertiary amine on the same support surface for efficient 1,4-addition reaction of phenylboronic acid.[2] In this study, we developed a new catalyst having high activity for hydrosilylation reaction due to the immobilized Rh complex and tertiary amine on the same SiO₂ surface (SiO₂/Rh-NEt₂). It can be expected that the hydrosilylation reaction is accelerated by electron donation from the tertiary amine to the Rh complex on the same surface. The catalyst showed excellent turnover number (TON) and wide substrate scope for the hydrosilylation of olefins.

The structure of SiO₂/Rh-NEt₂ was characterized by solid-state NMR, Rh K-edge XAFS, and elemental analysis. In the hydrosilylation reaction, SiO₂/Rh-NEt₂ showed higher activity than the catalyst with only Rh(I) complex, SiO₂/Rh (Figure 1). On the other hand, no target compound was produced when a catalyst, SiO₂/NEt₂, immobilized only with amine was used. These results suggest improvement in the catalytic activity of the rhodium complex by the tertiary amine present on the same surface.

Moreover, the TON of SiO₂/Rh-NEt₂ approached up to 1,900,000 (Scheme 1). This value is the highest compared to previously reported immobilized Rh catalysts.[3,4]

SiO₂/Rh-NEt₂ showed wide scope of substrate: the reaction of terminal olefins, such as 1-octene and allylbenzene, proceeded effectively to afford the corresponding hydrosilylation product in excellent yields. Not only simple terminal olefins but also olefins with functional groups such as a cyanoalkene and epoxyalkene reacted with hydrosilane in the presence of SiO₂/Rh-NEt₂.

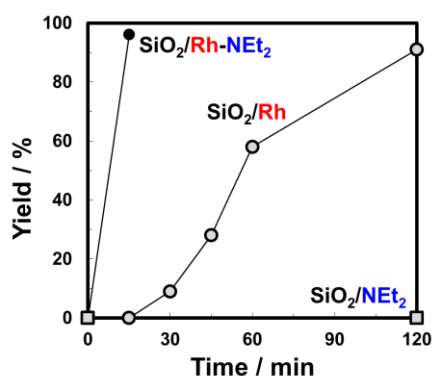
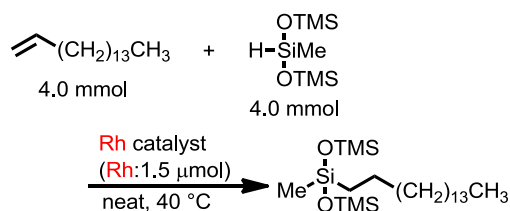
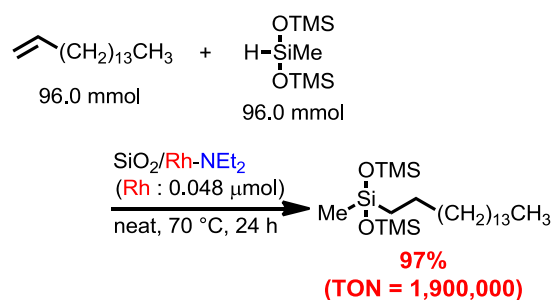


Figure 1 Accelerating action of hydrosilylation reaction using Rh catalyst with amine



Scheme 1 The maximum TON of hydrosilylation reaction with SiO₂/Rh-NEt₂

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