Co-immobilization procedure of Rh complex and tertiary amine on same SiO_2 surface for highly efficient hydrosilylation of olefins

Kyogo Maeda,[a] **Ken Motokura,**[a,]* **Yohei Uemura,**[b] **Daiju Matsumura,**[c] **Wang-Jae Chun**[d]
[a]*Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 226-8502, Japan*
[b]*Institute for Molecular Science, 38 Myodaiji-cho Nishigonaka, Okazaki, 444-8585, Japan*
[c]*Japan Atomic Energy Agency, Materials Sciences Research Center,1-1-1 Sayo-cho Koto, Sayo-gun, 679-5148, Japan*
[d]*International Christian University, 3-10-2 Osawa, Mitaka, 181-8585, Japan*
**Corresponding author: 045-924-5569, motokura@chemenv.titech.ac.jp*

Abstract: Co-immobilization of Rh complex and tertiary amine on same silica surface enhances hydrosilylation reaction of olefins. Here, the detailed co-immobilizing method, such as types of solvent and loading amount of functions, were investigated. As a result, the use of 1,4-dioxane instead of toluene as immobilization solvent improved its catalytic activity about 1.5 times. In addition, the relationship between the immobilization method and the Rh complex structure was analyzed by Rh K-edge XAFS measured at around 20 K.

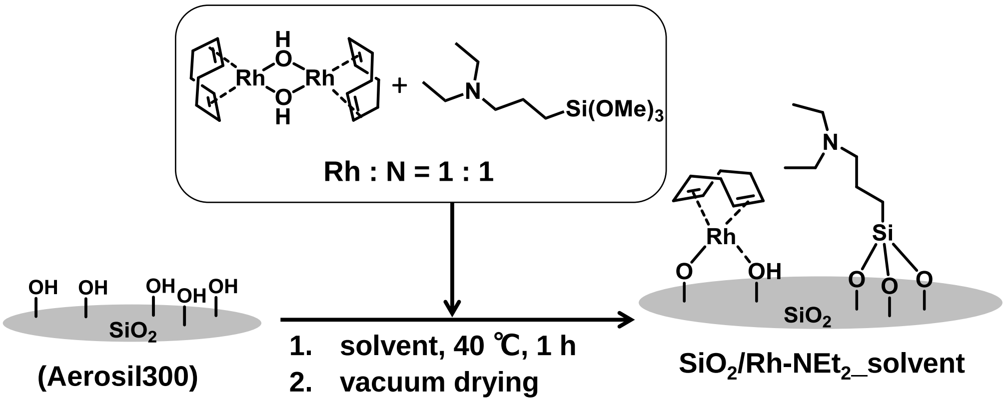
Keywords: co-immobilization, heterogeneous catalyst, Rh catalyst.

1. Introduction

The hydrosilylation is a reaction widely used for the synthesis of organosilicon compounds which are industrially useful intermediates and products. In 2008, Marciniec et al. reported Rh complex immobilized on silica surface[1]. This catalyst showed high activity for the hydrosilylation reaction. Also, in 2016, Lin and co-workers developed Rh complex attached on metal organic frameworks as a highly active and reusable catalyst for hydrosilylation[2]. In our group, it has been confirmed that the catalyst in which the Rh complex and the tertiary amine are present on the same SiO_2 surface shows higher activity in the hydrosilylation than only Rh complex on SiO_2[3]. The interaction between the Rh complex and tertiary amine in the precursor solution confirmed by CSI-MS spectrum indicated that these two functionalities are positioned closely on the SiO_2 surface, enabling the concerted activation of substrates. Herein, the detailed co-immobilizing method, such as types of solvent was investigated. In addition, Rh K-edge XAFS measurement at 20 K was conducted to determine the interaction of two functions on SiO_2.

2. Experimental

Scheme 1 represents preparation procedure of SiO_2-supported both Rh complex and tertiary amine in organic solvent (SiO_2/Rh-NEt_2_solvent). Rh complex and tertiary amine were simultaneously immobilized on SiO_2 surface using mixed solution of precursors.

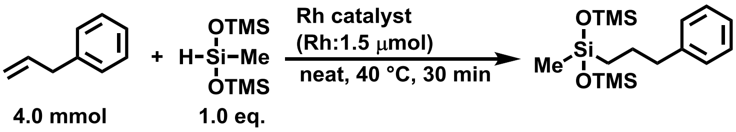


Scheme 1. Preparation of SiO_2/Rh-NEt_2_solvent

3. Results and discussion

Table 1 summarise the results of hydrosilylation of allylbenzene using SiO_2 supported Rh catalysts. The catalyst which includes the Rh complex and the amine showed higher activity than the catalyst only the Rh complex was immobilized. The use of 1,4-dioxane or cyclopentylmethylether instead of toluene as the immobilization solvent improved its catalytic activity more than 1.5 times. These results suggest that, at immobilization step, interaction between Rh complex and tertiary amine in the precursor solution is affected by types of solvent which influences to the catalytic activity. When the loading amount of Rh on the SiO_2/Rh-NEt_2_dioxane were changed (0.30 - 0.68 mmol/g), the catalytic activity were almost maintained. Even at low concentrations in precursor solution, two functions are immobilized in the proximity position by interaction between Rh complex and tertiary amine.

Table 1 Hydrosilylation Reaction with SiO_2/Rh and SiO_2/Rh-NEt_2



Entry	Rh catalyst	Yield[a]
1	0.48 mmol/g-SiO_2/Rh-NEt_2_toluene	40%
2	0.48 mmol/g-SiO_2/Rh-NEt_2_CPME[b]	61%
3	0.48 mmol/g-SiO_2/Rh-NEt_2_dioxane	64%
4	0.30 mmol/g-SiO_2/Rh-NEt_2_dioxane	73%
5	0.68 mmol/g-SiO_2/Rh-NEt_2_dioxane	73%
6	0.54 mmol/g-SiO_2/Rh_dioxane	trace

[a] Determined by ^{1}H NMR Yield. [b] cyclopentylmethylether

In order to exclude the effect of thermal vibration, XAFS measurement was performed at 20 K. Comparing Fourier transformed Rh K-edge EXAFS spectra measured at RT and 20 K, the latter shows clear signals at 2nd shell (2-3Å). The 2nd shell may be derived from four sp^3 carbon atoms of cyclooctadiene ligand of surface Rh complex, because the presence of cyclooctadiene ligand was also confirmed by NMR and FT-IR analysis. At SiO_2/Rh-NEt_2_dioxane, the bond length between Rh and atoms at 2nd shell are slightly shorter than SiO_2/Rh_dioxane. This result obtained by XAFS analysis infers that amines are present in the vicinity of the Rh complex on silica surface. It seems that the distance between Rh and carbon atoms of 2nd shell has approached due to steric repulsion between amines and cyclooctadiene ligand. The details will be discussed in presentation.

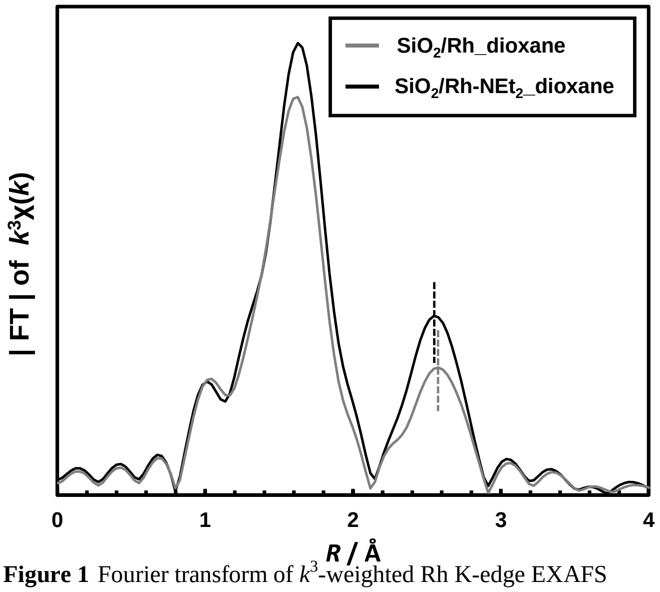


Figure 1 Fourier transform of k^3-weighted Rh K-edge EXAFS spectra at (a) RT and (b) 20 K

4. Conclusions

The relationship between the solvent used for immobilization and the catalytic activity was investigated. In the hydrosilylation reaction, the use of 1,4-dioxane instead of toluene as immobilization solvent improved its catalytic activity more than 1.5 times. According to the Rh K-edge EXAFS spectra measured at 20 K, the difference among the catalysts was found at bond length between Rh and atoms at secondary coordination sphere due to the interaction with amine.

References

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