1. Introduction

Hydrosilylation of olefins is an important process in the silicone industry. The reaction product, organosilane is an amphiphilic compound having both organic functional groups derived from olefins and the silyl functional group (Eq. (1)). Owing to this, it is possible to tune the functionality of the organosilicon products by selecting appropriate organic groups in the olefins and an appropriate structure of the hydrosilane substrate. The unique property and highly functionality of the organosilicon compounds increase their application towards organic-inorganic oils, silicone rubbers, surface coating regents, sealants, cosmetics, and also pharmaceuticals.

At present, Pt complexes are widely used as catalysts for hydrosilylation. However, the world Pt usage for this application amounts to 5.6 tons per year, with almost no recovery. When using a noble metal catalyst, it is urgent to reduce the amount of catalyst used. Therefore, the development of highly active and reusable industrial catalysts are desired.

In this review, the basic chemistry of hydrosilylation of olefins using metal complex catalysts is introduced first. Next, based on the reactivity and mechanism of such metal complex catalysts, homogeneous catalysts used in the industry as well as the recent advances in the hydrosilylation of olefins using heterogeneous catalysts are presented.

2. Chemistry of Hydrosilylation

Several mechanisms of hydrosilylation have been proposed. Scheme 1 represents the Chalk-Harrod mechanism involving (1) the coordination of olefin to metal complex and oxidative addition of hydrosilane, (2) the insertion of olefin to M-H bond, and (3) the reductive elimination of the hydrosilylation product, generating the organosilicon compound. This mechanism follows the anti Markovnikov rule.

In the modified Chalk-Harrod mechanism shown in Scheme 2, the reaction proceeds by the insertion of an olefin into an M-Si bond instead of a M-H bond, and the final product obtained is a Markovnikov product.
Seitz and Wrighton have reported that when Co is used as the catalyst, the reaction follows a different mechanism (Scheme 3). In the Seitz-Wrighton mechanism, a Si-C bond is formed by the insertion of an olefin into the M-SiR₃ bond originally contained in the metal complex. This is followed by the oxidative
addition of hydrosilanes, reductive elimination of alkylsilanes, and regeneration of the active species with silyl groups.

In general, when a Rh(I) complex is used in a reaction following the Chalk-Harrod or modified Chalk-Harrod mechanism, the reaction proceeds via a Rh(I)/Rh(III) catalytic cycle. However, in 1985, Perutz et al. proposed the existence of a Rh(V) species in the hydrosilylation reaction using complex 7). As shown in Scheme 4, irradiating Rh(I) complex (η^5-C₅H₅)Rh(C₂H₄)₂ (1) with light at low temperature led to the formation of (η^5-C₅H₅)Rh(C₂H₄)(SiR₃)H (2). This compound was readily available for hydrosilylation and contained all the key ligands for a reaction obeying the Chalk-Harrod mechanism.

It was revealed by nuclear magnetic resonance (NMR) spectroscopy that 1 also reacted at room temperature to produce 2 and 3 (Scheme 5). 3 is a Rh(V) complex with hydride and silyl groups. In addition, similar Rh(V) complex prepared using triisopropylsilane (HSiPr₃) was identified by infrared spectroscopy, ultraviolet-visible spectroscopy, NMR spectroscopy, and mass spectrometry after its isolation and purification.

Perutz et al. speculated that the Rh(V) complex is an intermediate in the hydrosilylation reaction using complex 2, and proposed the reaction mechanism shown in Scheme 6. This is also a new class of reaction mechanism for the metal complex-catalyzed hydrosilylation of olefins.

As shown in Schemes 1, 2, and 6, the metal-catalyzed hydrosilylation proceeds through the Rh(I)/Rh(III) or Rh(III)/Rh(V) catalytic cycle without the formation of any Rh(0) monomeric species. Additionally, during the catalytic cycle, a ligand was always found to coordinate to the Rh center. These facts suggested that the immobilization of an active metal such as Rh onto a support surface was possible by covalent or coordination bonding.

3. Industrial Process of Hydrosilylation

The first hydrosilylation reaction was reported in 1947 by Sommer et al. 8). The reaction was based on a radical chain mechanism, in which the activated Si-H bond by methyl radical from acetyl peroxide reacted with olefin. However, the yield and selectivity of the reaction was poor (the hydrosilylation product was obtained in 24% yield).

Subsequently, a heterogeneous Pt catalyst was reported by G. H. Wagner (1953) 9). Pt particles supported on powdered carbon behaved as the active species, and good performances were obtained (Scheme 7). However, the research and development on Pt catalysts was again diverted to homogeneous catalysts such as Speier’s catalyst (H₂PtCl₆) (1957) 10) and Karstedt’s catalyst (1973) 11). Today, Karstedt’s catalyst is used for the industrial hydrosilylation. The catalyst exhibits very high activity and broad substrate scope and generates no by-products (Scheme 8).

With the development of Pt catalysts, there are concerns about the reaction selectivity, catalyst cost, future catalyst supply, and reduction in the amount of usage of the catalysts. Therefore, reaction systems using other metal (Rh, Ir, Fe, Ru, Ni, Ti, Re) catalysts have been developed 12). Recently, hydrosilylation reactions using base metal elements, such as Fe, has been actively studied, and one of the homogenous Fe catalysts resulted in a turnover number (TON) of over 1000 13).

![Scheme 4](image-url) Generation of Rh(III) Intermediate from Rh(I) Complex

![Scheme 5](image-url) Generation of Rh(V) Intermediate from Rh(I) Complex

![Scheme 6](image-url) Perutz Mechanism for Olefin Hydrosilylation

![Scheme 7](image-url) Hydrosilylation with Pt/Catalyst

![Scheme 8](image-url)
4. Heterogeneous Catalysts for Hydrosilylation of Olefins

At present, the homogeneous Karstedt’s catalyst is primarily used for hydrosilylation. Although it has a high catalytic activity, the catalyst is not recoverable, and Pt is merely consumed in the reaction\(^\text{3}\). Considering the future industrial usage, there is a huge demand for the development of solid catalysts that can be easily recovered. The recent examples of solid (heterogeneous) catalysts used in the hydrosilylation of olefins are summarized in this section.

For hydrosilylation of alkynes and other unsaturated carbon-carbon bonds using heterogeneous metal catalysts, including supported metal complex and mono and bimetallic catalysts, have been also developed\(^\text{14}\). Recent examples are shown in reference \(^\text{14}\) and cited therein.

In 2016, Sawano et al. reported a metal organic framework (MOF)-supported Rh catalyst (P\(_1\)-MOF-Rh). The unit structure is shown in Fig. 1\(^\text{15}\). In this catalyst, the Rh complex is immobilized onto the MOF, which includes a monophosphine ligand as a unit. When the Rh complex is immobilized onto the MOF with a repeating structure, each Rh complex is located at an appropriate distance interval, resulting in no direct interaction between the Rh complexes. The complex is stable throughout the reaction and does not undergo disproportionation. However, when the monophosphine Rh complex is used in solution, the complex disproportionates into inactive metal Rh and diphosphine Rh complex. In the hydrosilylation reaction shown in Scheme 9, P\(_1\)-MOF-Rh catalyst showed high activity, and the TON reached 820,000 after 72 h.

In addition, it was confirmed that the reported catalyst exhibited high activity not only for the hydrosilylation of olefins, but also for various other catalytic reactions such as the hydrogenation of ketones and olefins with H\(_2\) and C-H borylation of arenes. Most importantly, the catalyst was stable, and the catalytic activity was maintained even after 10 cycles (Scheme 10). Corma and coworkers also reported hydrosilylation of styrene using recyclable supported Au complex and nanoparticles catalysts\(^\text{16}\).

In 2017, Beller et al. developed a heterogeneous single atom catalyst for the hydrosilylation reaction\(^\text{17}\). Recently, there has been an increasing number of reports on single atom catalysts, which include metals dispersed at the atomic level. Such catalysts are known to exhibit improved activity as compared with bulk and nanoparticle catalysts\(^\text{18}\). This catalyst was the first example of a single atom catalyst for the hydrosilylation reaction. For preparing the single atom platinum catalyst (Pt/NR-Al\(_2\)O\(_3\)-IP), an aluminum nanorod (NR-Al\(_2\)O\(_3\)) with a high specific surface area (S\(_{\text{BET}}\) = 330 m\(^2\)/g) was added to an aqueous solution of hexachloroplatinic acid (H\(_2\)PtCl\(_6\) \cdot 6H\(_2\)O aq.) and acetone, stirred at atmospheric pressure, and dried in vacuum. The single atom Pt catalyst prepared by impregnation precipitation (Pt/NR-Al\(_2\)O\(_3\)-IP) exhibited excellent catalytic activity that was comparable with that of Karstedt’s catalyst (Table 1). On the other hand, the Pt nanoparticle catalyst prepared by reductive precipitation (Pt/NR-Al\(_2\)O\(_3\)-RP) showed low activity.

The stability of the catalysts was confirmed from the recycling experiments. The yield of the product was 92 % with Pt/NR-Al\(_2\)O\(_3\)-IP even in the sixth cycle (total...
TON of 1.18 $\times 10^6$). High-resolution scanning transmission electron microscopy and X-ray absorption fine structure (XAFS) measurements confirmed that the state of the catalyst did not change after the recycle reactions. Very recently, single atom Pt catalyst on N-doped graphene has also been reported as a heterogeneous catalyst for hydrosilylation of terminal olefins with triethoxysilane 19). Pt(0) nanoparticle stabilized by silica network was also reported by Ciriminna and coworkers 20).

In 2008, Marciniec and coworkers reported that silica-supported Rh complex shows high activity for the hydrosilylation reaction (Scheme 11) 21a). The catalyst was a grafted Rh mononuclear complex formed by reacting Rh binuclear complexes with silanol groups. In-situ NMR measurements confirmed that the reaction proceeded without leaching of the Rh complex.

Following this, they developed a catalyst in which an originally mononuclear Rh complex was immobilized 21b). Rh phosphine siloxide complexes ($[(\text{SiR}^\prime)^3\text{Rh}(\text{cod})(\text{PR}_3)]$, $\text{R} = \text{Cy}, \text{Ph}, \text{iPr}$) were used as precursors and were immobilized on the silica surface. The structures of the synthesized catalysts were determined by solid state NMR ($^1\text{H}$, $^{31}\text{P}$). The catalysts showed excellent activity and recyclability for hydrosilylation reaction (Scheme 12).

Examination of the NMR spectrum of the catalyst in the presence of a substrate suggested that the reaction followed the mechanism shown in Scheme 13, and no Rh was leached. The proposed cycle follows the Chalk-Harrod mechanism.

In subsequent studies, anticipating the industrial use, they tried to modify the reaction of olefin substrates using octakis(hydridodimethylsiloxy)octasilsesquioxane as a model compound instead of siloxide polymer (Scheme 14) 21c). Rh catalyst 1 and Rh catalyst 2 showed excellent yields. Both the catalysts could be used repeatedly for 10 reactions when [silane] : [olefin] : [Rh] $= 1 : 1.2 : 5 \times 10^{-5}$ (total TON of 19.8 $\times 10^4$). Moreover, the total TON in these reactions reached 200,000.

Several research groups, including ours, have developed catalysts with multiple active sites on a solid surface 22). Organic moieties were immobilized close to the metal complex on the same support surface, and the catalytic activity was enhanced by the “concerted effect.” In 2017, our group reported a catalyst in which the Rh complex and a tertiary amine were present on the same SiO$_2$ surface (SiO$_2$/Rh-NEt$_2$) (Scheme 15) 23). Moreover, the TON of SiO$_2$/Rh-NEt$_2$ approached 1,900,000 (Scheme 16). The substrate scope of the reaction was also broad (Table 2): not only alkylsilanes, alkoxysilanes, and phenylsilanes but also allylbenzene derivatives, cyanoolefin, and epoxy olefin could be used as reactive substrates.

We investigated the effect of amines on the Rh complex by dynamic nuclear polarization-enhanced (DNP) solid-state $^{15}$N NMR spectroscopy and Rh K-edge
XAFS measurement at 20 K. It was found that the amine sterically interacts with the COD ligand in the Rh complex immobilized on the silica surface. In-situ FT-IR revealed that the reactivity of the COD ligand with hydrosilane was enhanced. It was concluded that the presence of an amine facilitated the COD dissociation from the Rh center\textsuperscript{24}).

5. Conclusion

The basics of metal-catalyzed hydrosilylation of olefins, catalytic systems for industry, and recent advances of heterogeneous metal catalysts were reviewed. In the history of the hydrosilylation reaction, the catalysts used for the industrial purposes contain Pt and are often homogeneous catalysts. Recently, several types of heterogeneous metal catalysts have been developed, including supported metal complexes and single atom catalysts. Since heterogeneous catalysts have many merits, they should be seriously targeted for development. It is also suggested here that the performance of the heterogeneous catalysts are comparable with that of the currently used industrial catalysts.

Both homogenous and heterogeneous catalysts often contain precious metals (Pt, Rh, Ir, Ru). Though increasing efforts are being taken to replace such precious metals by Fe, Ni, and Co in homogeneous catalysts, no remarkable development is seen for heterogeneous catalysts in this regard. In future, improvement in the activity of these catalysts and development of heterogeneous catalysts are expected.

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| R            | Rh Catalyst | Yield of product [%] | TON  |
|--------------|-------------|----------------------|------|
| \(\text{CH}_2\text{CH}_3\) | 1           | 99 (99, 99, 99, 99, 99, 99, 99, 99, 99, 99, 99) | 198,000 |
|              | 2           | 99 (99, 99, 97, 98, 98, 96, 92, 89, 94)         | 191,600 |
| \(\text{OMe}\) | 1           | 99 (99, 99, 99, 99, 99, 99, 99, 99, 99, 99, 99) | 198,000 |
| \(\text{C}_6\text{H}_5\text{OMe}\) | 2           | 99 (99, 99, 97, 99, 98, 95, 94, 94, 90)         | 193,200 |
| \(\text{O} \) | 1           | 99 (99, 99, 99, 99, 99, 99, 99, 99, 99, 99, 99) | 198,000 |
|              | 2           | 99 (99, 99, 99, 99, 99, 99, 99, 99, 99, 99, 99) | 198,000 |

|               | 1*          | 98 (99, 99, 99, 99, 99, 99, 99, 99, 99, 99, 99) | 197,800 |
|               | 2*          | 96 (98, 99, 99, 99, 99, 99, 99, 99, 99, 99, 99) | 197,200 |

Reaction conditions: \([\text{HSi}]=:[\text{CH}_2=\text{CH}]=:[\text{Rh}]=1:1:2:5 \times 10^{-5}; T = 100^\circ \text{C}; t = 1 \text{ h} (\ast 4 \text{ h}), \text{toluene}\)

Scheme 14  Model Reaction of Hydrosilylation of Olefins with Spherolites

Scheme 15  Effect of Aminie on the Same Surface

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Table 2  Substrate Scope of SiO2/Rh-NEt2-catalyzed Hydrosilylation

| R = \( \overset{\circ}{CH_2})_{13}CH \) | SiO2/Rh-NEt2 (Rh: 1.5 \( \mu \)mol) | neat, 40 °C |
|--------------------------------------|--------------------------------------|-------------|
| 4.0 mmol                             | 1.0 eq.                              |             |
| R = \( \overset{\circ}{CH_2})_{13}CH \) | \( \overset{\circ}{Si} \)MeSi(\( \overset{\circ}{EtO} \)) \( \overset{\circ}{Si} \)Me(\( \overset{\circ}{EtO} \)) \( \overset{\circ}{Si} \)
| TMS \( \overset{\circ}{Si} \)
| Me\( \overset{\circ}{Si} \)
| Me\( \overset{\circ}{Si} \) \( \overset{\circ}{EtO} \)
| Me\( \overset{\circ}{Si} \)
| \( t = 15 \text{ min} \)
| 99 %, [99 %] \( \text{[Isolated yield]} \)
| \( t = 15 \text{ min} \)
| 99 %, [99 %] \( \text{[Isolated yield]} \)
| \( t = 15 \text{ min} \)
| 99 %, [99 %] \( \text{[Isolated yield]} \)
| \( t = 30 \text{ min} \)
| 76 % \( \text{[Isolated yield]} \)
| \( t = 30 \text{ min} \)
| 82 % \( \text{[Isolated yield]} \)
| \( t = 30 \text{ min} \)
| 76 % \( \text{[Isolated yield]} \)
| \( t = 30 \text{ min} \)
| 82 % \( \text{[Isolated yield]} \)
| \( t = 30 \text{ min} \)
| 76 % \( \text{[Isolated yield]} \)
| \( t = 1 \text{ h} \)
| 83 %, [82 %] \( \text{[Isolated yield]} \)
| \( t = 1 \text{ h} \)
| 99 % \( \text{[Isolated yield]} \)
| \( t = 1 \text{ h} \)
| 83 %, [82 %] \( \text{[Isolated yield]} \)
| \( t = 1 \text{ h} \)
| 99 % \( \text{[Isolated yield]} \)
| \( t = 2 \text{ h} \)
| 71 % \( \text{[Isolated yield]} \)
| \( t = 2 \text{ h} \)
| 94 %, [91 %] \( \text{[Isolated yield]} \)
| \( t = 2 \text{ h} \)
| 99 %, [97 %] \( \text{[Isolated yield]} \)
| \( t = 2 \text{ h} \)
| 99 %, [98 %] \( \text{[Isolated yield]} \)
| \( t = 2 \text{ h} \)
| 98 %, [95 %] \( \text{[Isolated yield]} \)
| \( t = 2 \text{ h} \)
| 99 %, [98 %] \( \text{[Isolated yield]} \)
| \( t = 2 \text{ h} \)
| 99 %, [98 %] \( \text{[Isolated yield]} \)

\[ \text{[Isolated yield]} \]
要  旨

不均一系金属触媒によるオレフィンのヒドロシリル化反応

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オレフィンのヒドロシリル化反応は1947年に発見され，今日では私たちの生活を支える基幹技術となっている。ヒドロシリル化反応に現在使用されている触媒は均一系Pt錯体触媒であり，再利用可能かつ高活性な不均一系金属触媒の開発が強く望まれてきた。本総説では，ヒドロシリル化反応の基礎的な反応機構と現行の工業利用について概要をまとめるとともに，不均一系金属触媒の最近の研究動向について解説する。2000年代以降，オレフィンのヒドロシリル化反応において優れたリサイクル性を有する不均一系金属触媒が報告されている。これら不均一系触媒は，均一系触媒に匹敵する活性を示す。特に，MOF固定化錯体触媒や，金属単原子触媒といった革新的な触媒が次々に発表されており，これらの触媒では，表面に存在する触媒活性種が分子あるいは原子レベルで精密にデザインされている。これらの報告に加え，シリカ表面にRh錯体をグラフートした触媒と，表面での協同触媒作用によるヒドロシリル化反応における高活性発現についても併せて述べる。

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