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Allylsilylation of alkenes catalyzed by H^+-exchanged montmorillonite with water

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ABSTRACT

Proton-exchanged montmorillonite (H^+-montmorillonite) was found to be a heterogeneous catalyst for allylsilylation of alkenes with allylsilanes. A wide variety of aromatic and aliphatic alkenes were effectively converted to the corresponding allylsilylated products in 15–120 min at 60–100 °C using H^+-montmorillonite with *ca.* 1-2 wt% of water. The increasing of the amount of water drastically accelerated the allylsilylation of alkenes. For example, the reaction of *p*-chlorostyrene with allyltrimethysilane afforded 90% yield of the product for 15 min at 40 °C using H^+-montmorillonite with 8.8 wt% of water, whereas only 2% yield of the product was obtained with 1.3 wt% of water. However, the final product yields with H^+-montmorillonite with 1–2 wt% of water were higher than that with the 8.8 wt% of water. A reaction mechanism including the formation of a disilylpropyl cation was proposed. One possible explanation for the role of water is stabilization of the active disilylcation on the montmorillonite surface and/or edges via electron donation from water molecules.

1. Introduction

Carbosilylation is a green synthetic protocol because of the stability and low toxicity of organosilicon compounds compared with other organometallic compounds such as organolithium and organozinc [1]. Allylsilylation is one of the carbosilylation reactions that allows the installation of both the allyl and silyl groups onto an organic molecule. In the case of allylsilylation of alkenes with allylsilane, the reaction affords 5-silyl-1-pentene derivatives (Eq. (1)). The allylsilylation products have high potential as intermediates for organic synthesis, because the allyl and silyl groups can be transferred by various organic reactions, such as oxidation and coupling reactions [2].

(1)

Allylsilylation of alkenes using allylsilanes with aluminum trichloride as a Lewis acid catalyst was first reported in 1995 by Jung and Yoo's group [3,4]. Generally, allylsilanes act as nucleophilic reagents in organic reactions. Thus, electrophilic activation of an alkene molecule is first effective to introduce the allyl group. After the addition of the allyl group, immediate elimination of the silyl group and exchange between the silyl group and an electrophilic activator (acid catalyst) affords the allylsilylation product. This reaction pathway suggests that acidic materials would be effective catalysts for the allylsilylation.

Cation-exchanged montmorillonites have been found to be highly active heterogeneous Lewis and Brønsted acid catalysts for various organic reactions [5–10]. Allylsilylation of alkenes with allylsilanes was examined by our group using various heterogeneous and homogeneous acids. As a result, among the protonic acids evaluated, H^+-montmorillonite was found to be an excellent catalyst for allylsilylation of both aromatic and aliphatic alkenes [11,12].

Montmorillonite naturally possesses water molecules on its outer surface and in its interlayer space [13,14]. It can be expected that the water molecule affects montmorillonite-catalyzed reactions. For example, in the clay-catalyzed Diels–Alder reaction, the stereoselectivity of the product depends on the amount of residual water in the clay [15]. During the course of our investigation on the effect of water on the catalysis of allylsilylation by H^+-montmorillonite, we found that the reaction was significantly accelerated by the presence of a small amount of water [16].

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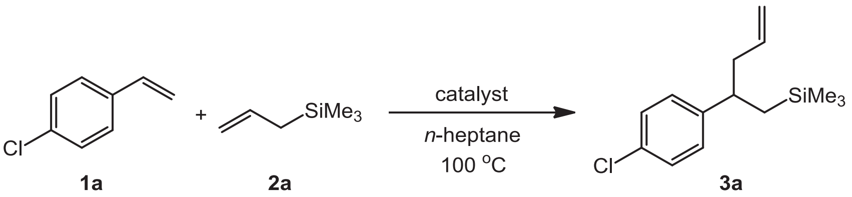
Table 1
Allylsilylation of *p*-chlorostyrene with allyltrimethylsilane using Brønsted acids.[a]



Entry	Catalyst	Conversion of alkene (%)[b]	Conversion of allylsilane (%)[b]	Yield (%)[b]
1	H^+-montmorillonite	99	55	85
2	MontK10	16	7	7
3	Na^+-montmorillonite	20	4	<1
4	H^+-USY	33	24	2
5	H^+-L	24	24	<1
6	H^+-mordenite	7	8	<1
7	H^+-beta	6	<1	<1
8	FSM-16	3	<1	<1
9	Amberlyst	20	25	<1
10	*p*-TsOH·H_2O[c]	15	11	<1
11	H_2SO_4[c]	5	9	<1

[a] Reaction conditions: *p*-chlorostyrene (**1a**: 1.0 mmol), allyltrimethylsilane (**2a**: 3.0 mmol), catalyst (0.10 g), *n*-heptane (1.0 mL), 100 °C and 30 min.
[b] Determined by GC using internal standards. Yield was based on *p*-chlorostyrene used.
[c] 0.1 mmol of acid was used.

In this paper, we summarize the results for the H^+-montmorillonite-catalyzed allylsilylation of alkenes. The relationship between the amount of adsorbed water and catalytic performance in the allylsilylation of alkenes is discussed. We also report the role of water molecules in the catalytic allylsilylation.

2. Experimental

2.1. Characterization procedures

Proton nuclear magnetic resonance (^1H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded in $CDCl_3$ with Jeol JNM-AL300 and Bruker AVANCE III 400 spectrometers operating at 300 and 75 MHz, or 400 and 100 MHz, respectively. Thermal gravimetric differential thermal analysis (TG-DTA) was performed using a Shimadzu DTG-60 with a heating rate of 5 K min^{-1} under a N_2 flow of 100 mL min^{-1}, from room temperature. Powder X-ray diffraction (XRD) patterns were measured using a RigakuDenki Multi Flex diffractometer with Cu Kα radiation, at 40 kV and 40 mA at a rate of 0.5° (2θ) per minute.

Analytical GLC was measured using a Shimadzu GC-7A equipped with a Silicon SE-30 column and a flame ionization detector. Shimadzu QP5000 was used as GC–MS equipped with DB-1 column.

2.2. Materials

Na^+-montmorillonite [$Na_{0.66}(OH)_4Si_8(Al_{3.34}Mg_{0.66}Fe_{0.19})O_{20}$; Kunipia F] was obtained from Kunimine Industry. Proton-exchanged montmorillonite (H^+-montmorillonite) was prepared from Na^+-montmorillonite using a previously reported ion exchange procedure with aqueous hydrogen chloride [17,18]. Physicochemical properties, such as acid amount (0.86 mmol g^{-1}), strength (ΔH = 111 kJ mol^{-1}), and concentration (6.3×10^{-3} mmol m^{-2}), of the H^+-montmorillonite were reported in the literature [17,18]. After the drying of H^+-montmorillonite at 110 °C, the amount of adsorbed water was *ca.* 1–2 wt%. Unless otherwise noted, H^+-montmorillonite was used without further treatment.

The procedure to produce the H^+-montmorillonite with different amount of adsorbed water is as follows. The parent H^+-montmorillonite was stored under 30% humidity for at least one week. H^+-montmorillonites with different amounts of adsorbed water were prepared as follows: the parent H^+-montmorillonite was dried under vacuum (*ca.* 1 mmHg) at the required temperature for 1 h before the catalytic reaction.

MontK10 was purchased from Aldrich. H^+-Beta (SiO_2/Al_2O_3 = 25), H^+-L (SiO_2/Al_2O_3 = 6.3), H^+-USY (SiO_2/Al_2O_3 = 5.9), and H^+-Mordenite (SiO_2/Al_2O_3 = 18.0) were purchased from Nikki Chemical Co. These zeolites were heated at 500 °C under air before use. FSM-16 was purchased from FUJI SYLYSIA Co. Amberlyst was purchased from Organo Co. as Amberlyst® 15DRY. Unless otherwise noted, all other materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto Kagaku Co., and Aldrich Inc.

2.3. Procedure for allylsilylation

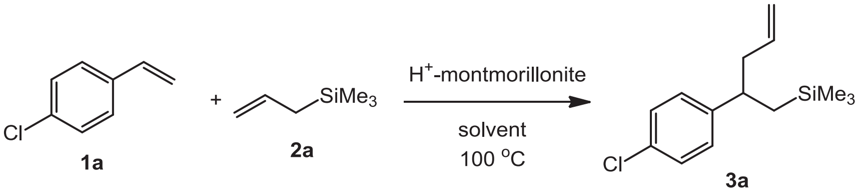
Procedure for allylsilylation of *p*-chlorostyrene (**1a**) with allyltrimethylsilane (**2a**) is as follows. H^+-montmorillonite (0.10 g), toluene (1.0 mL), **1a** (1.0 mmol), and **2a** (3.0 mmol) were placed into a glass reactor under a dry Ar atmosphere using Schlenk techniques. The resulting mixture was vigorously stirred at 100 °C. After 180 min, the catalyst was separated by filtration. GC analysis of the filtrate showed a 95% yield of [2-(4-chlorophenyl)pent-4-enyl]trimethylsilane (**3a**). The filtrate was evaporated and the crude product was purified by column chromatography using silica (*n*-hexane elute) to afford the pure product. The product was identified by ^1H and ^{13}C NMR and mass spectral data. Detailed reaction conditions are shown in Table footnote.

3. Results and discussion

3.1. Catalytic performances of H^+-montmorillonite

Allylsilylation of *p*-chlorostyrene (**1a**) with three equivalents of allyltrimethylsilane (**2a**) was carried out at 100 °C using various heterogeneous and homogeneous protonic acids. The results are shown in Table 1. H^+-montmorillonite showed the highest catalytic performance to give [2-(4-chlorophenyl)pent-4-enyl]trimethylsilane (**3a**) in 85% yield based on **1a** (entry 1). The product yield using commercially available montK10 was much lower than that for the H^+-montmorillonite (entry 2). The

Table 2
Allylsilylation of *p*-chlorostyrene with allyltrimethylsilane using H$^+$-montmorillonite in various solvents.[a]



Solvent	Conversion of alkene (%)[b]	Yield (%)[b]
Toluene	99	95[c]
Toluene	95	90
n-Heptane	99	85
1,4-Dioxane	12	2
Isopropanol	15	<1
DMF	6	<1
DMSO	<1	<1

[a] Reaction conditions: H$^+$-montmorillonite (0.10 g), **1a** (1.0 mmol), **2a** (3.0 mmol) solvent (1.0 mL), 100 °C and 30 min.
[b] Determined by GC using internal standard technique. Yield was based on *p*-chlorostyrene.
[c] 120 min.

product did not form when using sodium-exchanged montmorillonite (entry 3). Zeolites, such as USY and mordenite, were less active (entries 4–7). The reaction also did not proceed with *p*-toluenesulfonic acid and H_2SO_4 (entries 10 and 11).

The conditions for the H$^+$-montmorillonite-catalyzed reaction of **1a** with **2a** were optimized with respect to the solvent, as shown in Table 2. Toluene was found to be a better solvent than *n*-heptane, affording a 95% yield of **3a**. 4-[(Trimethylsilyl)methyl]-6-silahept-1-ene, a dimerized product of **2a**, was also detected in 16% yield based on the amount of **2a** used. An 86% yield of **3a** was obtained with toluene, even in the presence of two equivalents of **2a**. Allylsilylation did not proceed in polar solvents, such as dioxane and DMF. The substrate ratio was also investigated as shown in Table 3. The best yield of the product was obtained with alkene/allylsilane ratio of 1.0/3.0. The yield decreased upon decreasing the amount of allylsilane.

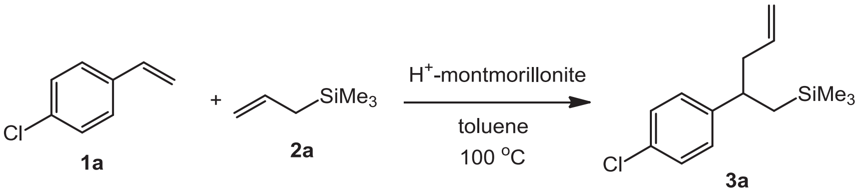
After the reaction, the H$^+$-montmorillonite could be easily recovered from the reaction mixture by filtration. In the reuse experiment, the catalytic activity decreased slightly; however, up to 70% yield of the product was obtained by prolonged reaction time at least 3rd use (Table 4).

The scope of substrates is shown in Table 5. The allylsilylation occurred with simple styrene to give the corresponding product in 72% yield. The H$^+$-montmorillonite-catalyzed reactions of other *p*-substituted styrenes, such as *p*-bromo, and *p*-fluorostyrenes, with **2a** afforded the corresponding allylsilylated products in 87 and 91% yields, respectively. This is the first report of the allylsilylation of styrene derivatives with allylsilane. Styrenes with electron-donating groups, such as *p*-methoxystyrene and *p*-methylstyrene, did not work well as substrates. H$^+$-montmorillonite also promoted the allylsilylation of aliphatic alkenes, such as 1-hexene, with **2a**. In addition to **2a**, allyltriethylsilane and methallyltrimethylsilane were also found to be good allylsilylating reagents.

Next, the effect of adsorbed water on the montmorillonite surface on the catalytic performance of the allylsilylation was investigated. The amount of adsorbed water was determined by thermal gravimetric analysis (TGA) [16]. Aliouane and co-workers have reported that the two periods of weight loss below 100 °C and between 100 and 150 °C during TGA are assignable to weakly linked water and H$^+$-coordinated water (H_3O^+), respectively [14]. Based on the TGA results, the amounts of water on the H$^+$-montmorillonites treated at different temperatures were determined as 5.6, 2.1, and 1.3 wt%, respectively (Table 6). These H$^+$-montmorillonites are denoted as H$^+$-montmorillonite-(5.6), -(2.1), and -(1.3), respectively. Differential thermal analysis (DTA) curves of the H$^+$-montmorillonites showed an endothermic peak below 150 °C. This result confirms that the weight loss below 150 °C corresponds to adsorbed water [16]. Maintenance of the layered structure of H$^+$-montmorillonite after the heat treatment was confirmed by X-ray diffraction (XRD) measurements [16].

To clarify the effect of water on the catalytic activity of H$^+$-montmorillonite in the allylsilylation reaction, allylsilylation of *p*-chlorostyrene with allyltrimethylsilane was carried out. Fig. 1 shows the time course of the product yield. Catalytic activity increased with the amount of adsorbed water

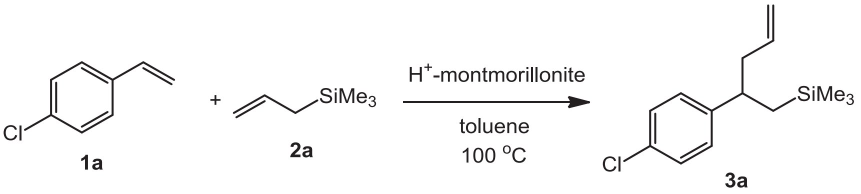
Table 3
Allylsilylation of *p*-chlorostyrene with allyltrimethylsilane using H$^+$-montmorillonite with various alkene/allylsilane ratios.[a]



Alkene/allylsilane (mmol/mmol)	Conversion of alkene (%)[b]	Yield (%)[b]
1.0/3.0	95	90
1.0/2.0	96	89
1.0/1.0	89	53

[a] Reaction conditions: H$^+$-montmorillonite (0.10 g), toluene (1.0 mL), 100 °C and 30 min.
[b] Determined by GC using internal standard technique. Yield was based on *p*-chlorostyrene.

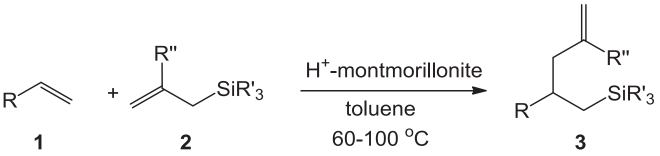
Table 4
Reuse of H$^+$-montmorillonite for allylsilylation of *p*-chlorostyrene with allyltrimethylsilane.[a]

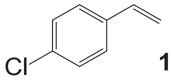
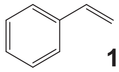
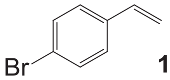
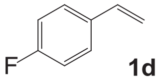
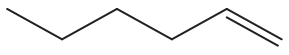
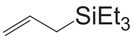
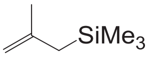


Reuse	Reaction time (min)	Conversion of alkene (%)[b]	Yield (%)[b]
Fresh	30	95	90
1st use	60	92	88
2nd use	120	87	77
3rd use	120	81	73

[a] Reaction conditions: H$^+$-montmorillonite (0.10 g), **1a** (1.0 mmol), **2a** (3.0 mmol), toluene (1.0 mL), 100 °C and 30 min.
[b] Determined by GC using internal standard technique. Yield was based on *p*-chlorostyrene.

Table 5
Allylsilylation of alkenes (**1**) with allylsilanes (**2**) using H$^+$-montmorillonite catalyst.[a]



Alkene	Allylsilane	**1/2** (mmol/mmol)	Time (min)	Conversion of **1** (%)[b]	Yield (%)[b]
 **1a**	**2a**	1.0/3.0	120	99	95
 **1b**	**2a**	1.0/3.0	15	93	72[c]
 **1c**	**2a**	1.0/3.0	30	96	87[d]
 **1d**	**2a**	1.0/3.0	60	98	91
 **1e**	**2a**	3.0/1.0	60	97[e]	88[f]
 **1f**	**2a**	3.0/1.0	60	99[e]	55[f]
1a	 **2b**	1.0/3.0	30	99	61
1a	 **2c**	1.0/3.0	30	99	86

[a] Reaction conditions: H$^+$-montmorillonite (0.10 g), toluene (1 mL) and 100 °C.
[b] Determined by GC using internal standard technique. Yield was based on alkene **1**.
[c] 5.0×10^{-2} g of H$^+$-montmorillonite was used.
[d] 80 °C.
[e] Conversion of allylsilane **2a** was shown.
[f] Reaction carried out at 60 °C. Yield was based on allylsilane **2a**.

[H$^+$-montmorillonite-(1.3) < -(2.1) < -(5.6)]. Next, allylsilylation using H$^+$-montmorillonite-(1.3) was carried out in the presence of additional water. The reaction rate in the initial period was increased by a factor of 60 by the addition of 7.5 mg of water to the reaction mixture including 0.10 g of H$^+$-montmorillonite-(1.3) (■) compared with no additional water (□). When the amount of water was increased to 50 mg (2.8 mmol), an induction period was observed in the allylsilylation, as shown in Fig. 2. During the

Table 6
Amount of adsorbed water and interlayer distance of H$^+$-montmorillonites treated at different temperatures.

Catalyst	Treatment temp. (°C)	Adsorbed water (wt%)[a]	Interlayer distance (Å)[b]
H$^+$-montmorillonite-(5.6)	25	5.6	3.4
H$^+$-montmorillonite-(2.1)	100	2.1	2.6
H$^+$-montmorillonite-(1.3)	120	1.3	2.4

[a] Determined by TG analysis.
[b] Determined by subtracting the *c* dimension of the silicate sheet (9.6 Å) from the observed d_{001} values in the XRD spectrum.

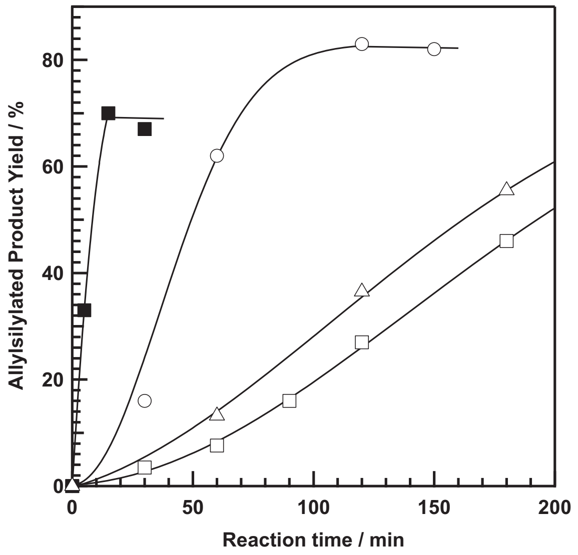


Fig. 1. Time course for allylsilylation of *p*-chlorostyrene with allyltrimethylsilane using (□) H^+-montmorillonite-(1.3), (△) H^+-montmorillonite-(2.1), (○) H^+-montmorillonite-(5.6), and (■) H^+-montmorillonite-(1.3) with 7.5 mg of H_2O (total: 8.8 wt%). Reaction conditions: *p*-chlorostyrene (1.0 mmol), allyltrimethylsilane (3.0 mmol), H^+-montmorillonite (0.10 g), toluene (1.0 mL), 50 °C.

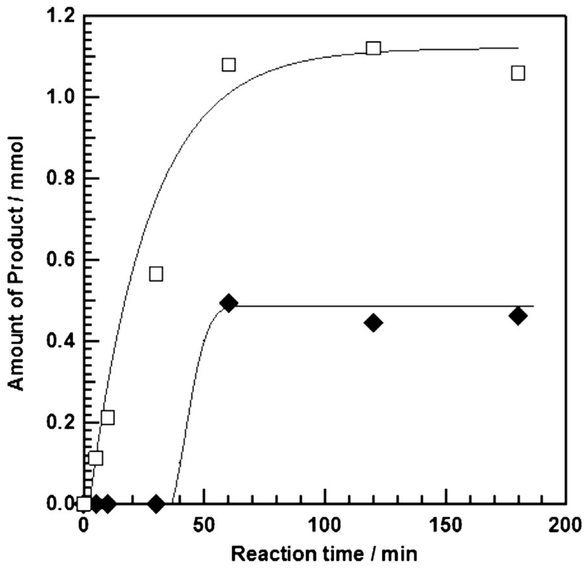


Fig. 2. Time course for the amount of allylsilylationproduct (◆) and hexamethyldisiloxane (□). Reaction conditions: H^+-montmorillonite-(1.3) (0.10 g), *p*-chlorostyrene (1.0 mmol), allyltrimethylsilane (3.0 mmol), toluene (1.0 mL), H_2O (50 mg) and 50 °C.

induction period, the formation of *ca.* 1.0 mmol of hexamethyldisioxane ($Me_3SiOSiMe_3$) was observed. In other words, *ca.* 0.5 mmol of water was consumed during the induction period by the reaction with allyltrimethylsilane to give $Me_3SiOSiMe_3$. Results shown in Figs. 1 and 2 indicated that the presence of an appropriate amount of water for the allylsilylation.

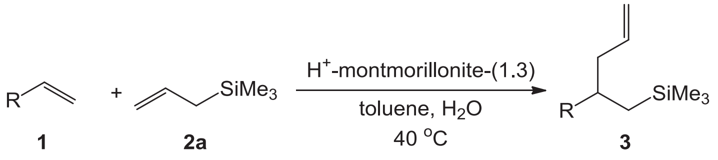
The allylsilylation of various alkenes was examined using H^+-montmorillonite-(1.3) with additional H_2O, and the results are summarized in Table 7. H^+-montmorillonite contains 8.8 wt% of water after the addition of 7.5 mg of water to the 0.10 g of H^+-montmorillonite-(1.3). The reactions of styrenes having electron-withdrawing groups proceeded at 40 °C. For example, the reaction of *p*-chlorostyrene was completed within 15 min, giving a 90% yield of the product, while a yield of only 2% was obtained without the additional H_2O under the same reaction conditions. The reaction of styrene with allyltrimethylsilane was also accelerated by the addition of H_2O. In the case of H^+-montmorillonite with 1–2 wt% of water, as shown in Table 5, high reaction temperatures (60–100 °C) and long reaction times (15–120 min) were necessary to complete the allylsilylation of various alkenes. In contrast, the allylsilyaltion completed in 15–60 min at 40 °C using H^+-montmorillonite with 8.8 wt% of water due to the much faster reaction rate (Table 7). However, the final product yields were slightly lower than in the case of no additional water (Table 5). For example, the final yields from 1-hexene (**1e**) with and without the additional water were 88 (Table 5) and 64% (Table 7), respectively. The presence of water induced decomposition of allylsilane, resulting in the low final yield of the allylsilylation product.

3.2. *Investigation of reaction mechanism*

In order to elucidate the H^+-montmorillonite-catalyzed reaction pathway, we examined the reaction of cyclohexene with allyltrimethylsilane (**2a**). ^1H NMR study revealed the formation of the allylsilylated product with exclusively *trans* allyl and silyl groups (Scheme 1). There were no other major products converted from cyclohexene. This result suggests stepwise addition of the silyl and allyl groups of the allylsilane to the alkenes [3,4].

Jung and co-workers proposed a reaction mechanism for the $AlCl_3$-catalyzed allylsilylation of alkenes, which involves a cationic silane intermediate, a 1,3-disilylpropyl cation ($SiCH_2C^+HCH_2Si$)

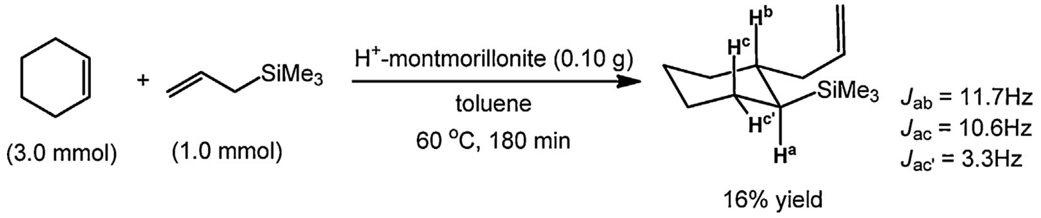
Table 7
Allylsilylation of alkenes with allyltrimethylsilane using H^+-montmorillonite-(1.3) at 40 °C.[a]



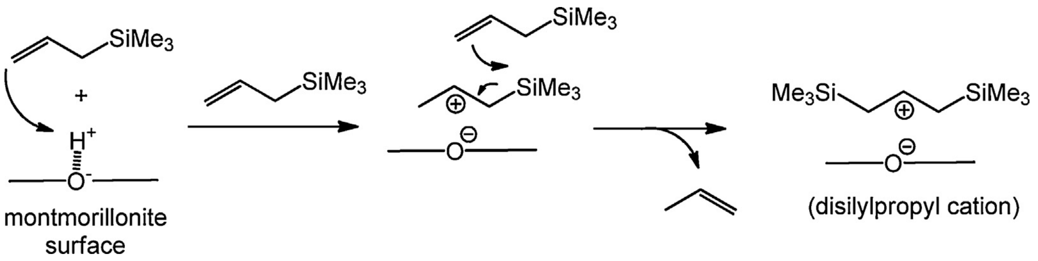
Alkene (R=)	Time (min)	Additional H_2O (mg)	Conversion of alkene (%)[b]	Yield (%)[b]
p-Cl-Ph-(**1a**)	15	7.5	93	90
p-Cl-Ph-(**1a**)	15	0	2	2
p-F-Ph (**1d**)	15	7.5	91	81
p-Br-Ph-(**1c**)	60	7.5	99	74
Ph-(**1b**)	15	7.5	95	55
Ph-(**1b**)	15	0	4	2
n-C_4H_9-(**1e**)	15	7.5	96	64

[a] Reaction conditions: alkene (1.0 mmol), allyltrimethylsilane (3.0 mmol), H^+-montmorillonite (0.10 g), toluene (1.0 mL) and 40 °C. H^+-montmorillonite was treated at 120 °C under vacuum before the reaction (H^+-montmorillonite-(1.3)). After 10 min, 1.0 mmol of additional allylsilane was added.

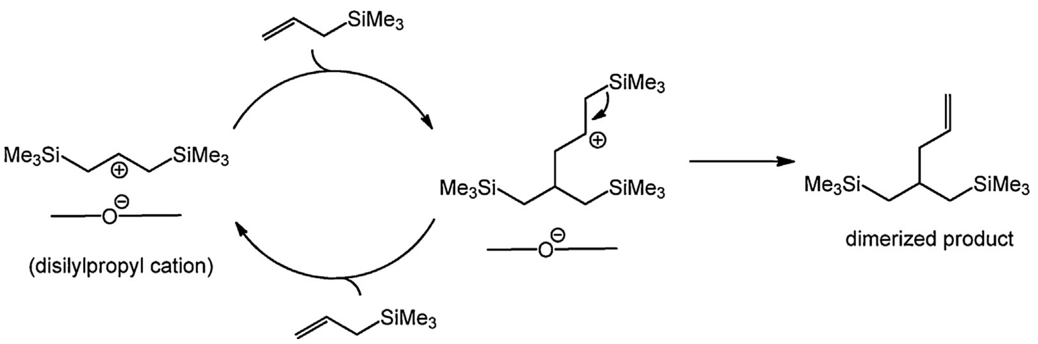
[b] Determined by GC and ^1H NMR using internal standard technique.



Scheme 1. Allylsilylation of cyclohexene with allyltrimethylsilane using H+-montmorillonite.

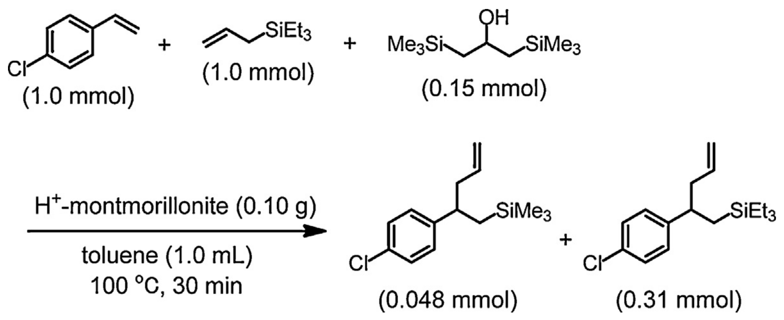


Scheme 2. Possible pathway for 1,3-disilylpropyl cation formation from allyltrimethylsilane and H+-montmorillonite.

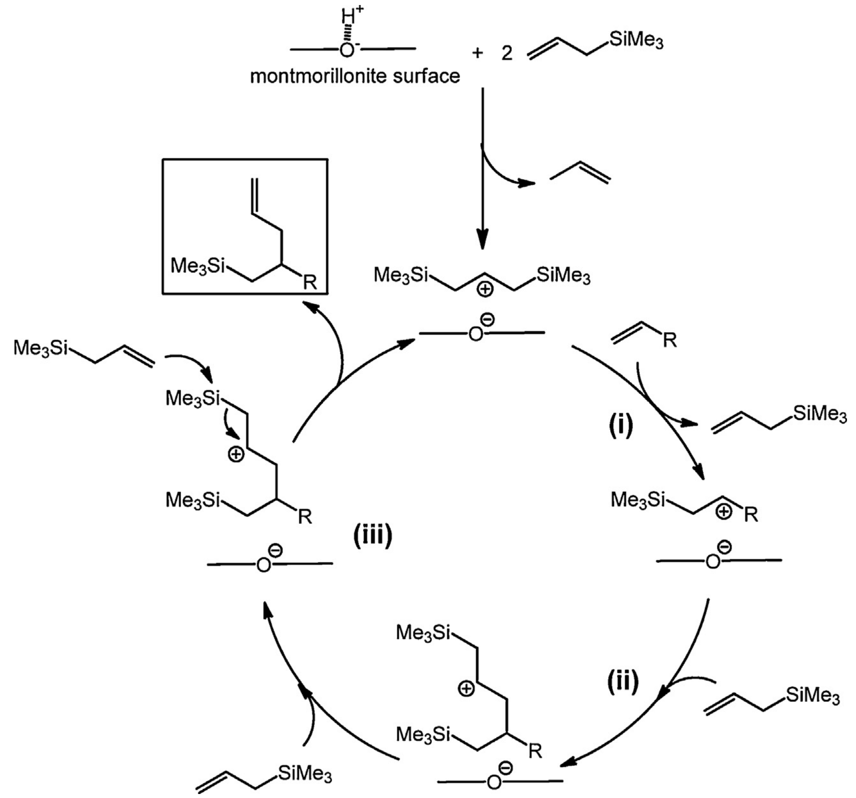


Scheme 3. Estimated pathway for dimerization of allyltrimethylsilane on montmorillonite surface.

[3]. A possible pathway of formation of the 1,3-disilylpropyl cation from **2a** and H+-montmorillonite is shown in Scheme 2. Formation of propylene by reaction of allylsilane with H+-montmorillonite also supports this pathway. During the treatment of H+-montmorillonite with allyltrimethylsilane, the dimerization of allyltrimethylsilane took place. The dimerized product is thought to be obtained from the reaction of the 1,3-disilylpropyl cation with allyltrimethylsilane (Scheme 3). To confirm the participation of the 1,3-disilylpropyl cation in the catalytic allylsilylation of alkenes, reaction of **1a** with allyltri*ethyl*silane was examined in the presence of 1,3-di(trimethylsilyl)propan-2-ol, a precursor to the 1,3-disilylpropyl cation. After the reaction, the formation of an allylsilylated product with a $SiMe_3$ group was observed (Scheme 4). These results suggest that the 1,3-disilylpropyl cation forms from allylsilane on the montmorillonite surface, and acts as a reaction intermediate. Thus, a catalytic cycle for the allylsilylation of alkenes using H+-montmorillonite is proposed, as shown in Scheme 5: (i) nucleophilic attack of an alkene to a disilylcation to form allylsilane and a secondary carbocation intermediate stabilized by the silyl group at the β-position, (ii) nucleophilic attack of an allylsilane to the intermediate to form a new C—C bond, and (iii) formation of allylsilylated product and disilylcation by nucleophilic addition of another allylsilane. To determine the rate-determining step, the allylsilylation was conducted at 50 °C with various *p*-chlorostyrene concentrations. Reaction conditions are as follows: H+-montmorillonite (0.10 g), toluene (1.0 mL), *p*-chlorostyrene (1.0, 2.0, and 3.0 mmol), and allyltrimethylsilane (3.0 mmol). In all cases, the product yields were *ca.* 10% at



Scheme 4. Allylsilylation of *p*-chlorostyrene with allyltri*ethyl*silane in the presence of 1,3-disilylpropan-2-ol.



Scheme 5. Proposed catalytic cycle for the allylsilylation of alkenes with allylsilane using H^+-montmorillonite.

1.5 h. The rate of allylsilylation at low conversion (<10%) was almost independent of the *p*-chlorostyrene concentration. The electron-withdrawing substitution of *para*-position of styrene enhanced the allylsilylation rate. These results indicate that nucleophilic addition of allylsilane (step (ii) or (iii)) is included in the rate-determining step.

3.3. *Role of adsorbed water*

The interlayer space of montmorillonite expands slightly in nonpolar solvents. However, this expanded interlayer space is not sufficient to allow the entrance and reaction of organic molecules. The allylsilylation reaction proceeded in nonpolar solvents, such as toluene and *n*-heptane. As shown in Table 6, the interlayer distances of the H^+-montmorillonites (2.4–3.4 Å), which correspond to the sizes of H_2O and H_3O^+, are too narrow to allow the entrance of *p*-chlorostyrene and allyltrimethylsilane molecules. These facts indicate that differences in the interlayer distances of the H^+-montmorillonites (Table 6) do not affect their catalytic performances in the allylsilylation reaction.

To investigate the interaction between the Si group and the water molecule, the reaction using allyltri*ethyl*silane was examined using H^+-montmorillonite-(1.3) with and without the addition of H_2O at 40 °C, as shown in Table 8. The reaction of *p*-chlorostyrene with allyltriethylsilane was accelerated by the addition of H_2O, however, the accelerating effect was much smaller than in the reaction of allyltrimethylsilane. Due to the bulky ethyl group on the Si atom, the interaction between the $SiEt_3$ group and the H_2O molecule is much weaker compared with that of the $SiMe_3$ group. This suggests that the interaction between the Si atom and H_2O (Scheme 6) plays a key role in the acceleration of the allylsilylation.

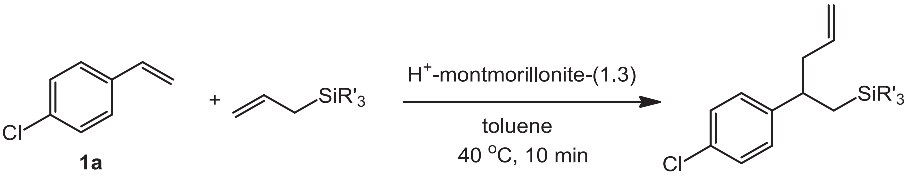
If the carbocation center is more electrophilic than the silyl group of the disilylcation, 1,3-bis(trimethylsilyl)-2-propanol should form in the presence of H_2O. Upon careful analysis of the reaction mixture by GC–MS, however, 1,3-bis(trimethylsilyl)-2-propanol was not detected. This indicates that the Si center is more electrophilic in the disilylcation. Because Si atom shows high affinity for oxygen atom, the H_2O molecule might interact with the Si atom of the cationic species. The formation of silanol and disiloxane as byproducts (Fig. 2) also supports this hypothesis.

As shown in Scheme 5, all cationic intermediates include $SiMe_3$ group. Since the interaction between H_2O and $SiMe_3$ group is an election donation from H_2O to Si atom, the rate-determining step (Scheme 5, (ii) or (iii)) cannot be accelerated by such interaction. One possible explanation for the role of water is stabilization of the active disilylcation on the montmorillonite surface and/or edges via electron donation from the water molecules to increase the concentration or life time of active species, as shown Scheme 6. We have previously reported the formation of inactive $SiMe_3$ species on the montmorillonite surface after the catalytic reaction [11,16]. This is a reason for the gradually decreasing of the catalytic activity during reuse experiment (Table 4). The water may suppress such deactivation pathway.

As shown in Scheme 6, at least two H_2O molecules could interact with the possible cationic silyl species. Table 9 summarizes amount of H_2O, H_2O/H^+ site ratio, and reaction rate for the allylsilylation of *p*-chlorostyrene with allyltrimethylsilane in each catalytic system. At least five times more water than acid sites are necessary to promote the catalytic allylsilylation significantly. This is a reasonable value because two types of H_2O molecules can be observed on the montmorillonite surface: (i) H_2O close to the H^+ site and (ii) weakly linked water on the montmorillonite surface [14].

The possibility of abstraction of $SiMe_3$ group from cationic intermediate (iii) (Scheme 5) by H_2O molecule cannot be completely

Table 8
Allylsilylation of *p*-chlorostyrene with allyltrimethylsilane or allyltriethylsilane with and without additional H_2O.[a]



Allylsilane (SiR'_3=)	Product yield (%)[b]	
	With additional H_2O[c]	Without additional H_2O
$SiMe_3$	73	<1
$SiEt_3$	8	<1

[a] Reaction conditions: alkene (1.0 mmol), allyltrimethylsilane (3.0 mmol), H^+-montmorillonite (0.10 g), toluene (1.0 mL), 40 °C and 10 min. H^+-montmorillonite was treated at 120 °C under vacuum before the reaction (H^+-montmorillonite-(1.3)).

[b] Determined by ^1H NMR using internal standard technique.

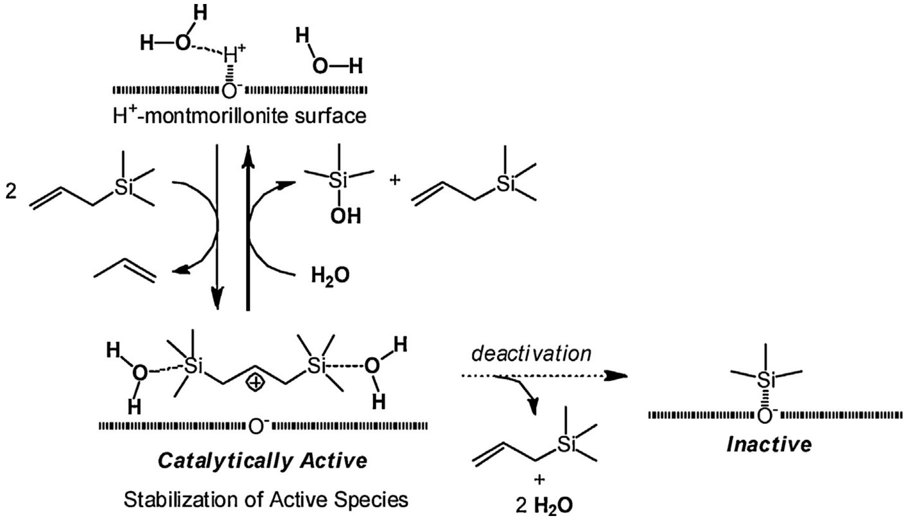
[c] H_2O (7.5 mg).

Table 9
Effect of H_2O/acid site molecular ratios on the rate of the allylsilylation catalyzed by H^+-montmorillonite.

Catalyst and additive	Amount of H_2O (mmol)	H_2O/acid site[a]	Rate (mmol/min)[b]
H^+-montmorillonite-(1.3)	0.072	0.83	1.0×10^{-3}
H^+-montmorillonite-(2.1)	0.12	1.4	1.8×10^{-3}
H^+-montmorillonite-(5.6)	0.31	3.6	1.3×10^{-2}
H^+-montmorillonite-(1.3) + 7.5 mg of H_2O (total: 8.8 wt%)	0.49	5.7	6.6×10^{-2}

[a] Amount of acid site in 0.10 g of H^+-montmorillonite is calculated to be 0.086 mmol.

[b] Reaction conditions: *p*-chlorostyrene (1.0 mmol), allyltrimethylsilane (3.0 mmol), H^+-montmorillonite (0.10 g), toluene (1.0 mL) and 50 °C.



Scheme 6. Proposed roles of water: stabilization of the catalytically active species.

ruled out. In this case, silanol and/or disiloxane formation occurs, and a stoichiometric amount of H_2O is consumed. In fact, the formation of both silanol and disiloxane was detected. However, the abstraction of $SiMe_3$ group by H_2O is not the primal reason for the acceleration effect by water due to following reasons.

In Scheme 4, the ratio of $SiMe_3$ and $SiEt_3$ group in substrates (allylsilane and alcohol) and products are very close. This result indicates that the rapid exchange of silyl groups between a cationic intermediate and an allylsilane occurs during the catalytic cycle. This fact indicates that step (iii) in Scheme 5, the Si exchange reaction, proceeds more rapidly than the C—C bond formation step (ii). This fact indicates that step (ii) is the rate-determining step in the allylsilylation. This conclusion supports that the abstraction of $SiMe_3$ by H_2O, which can accelerate step (iii), should not be the primal reason for the acceleration of allylsilylation.

4. Conclusion

H^+-montmorillonite was found to be an active catalyst for the allylsilylation of alkenes with allylsilanes at 60–100 °C without additional water. Styrene derivatives having electron-withdrawing groups and aliphatic alkenes can be used as alkene substrates. The catalyst can be reused at least three times with maintenance of the high product yields. Addition of 7.5 wt% of water to the 0.10 g of H^+-montmorillonite improved the catalytic activity: the allylsilylation of almost all alkenes completed within 15 min at 40 °C.

However, the final product yields were slightly lower than in the case of no additional water. Experimental results suggest that an interaction between the water molecule and $SiMe_3$ stabilizes the active intermediate.

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