ACS Catalysis
Letter
pubs.acs.org/acscatalysis

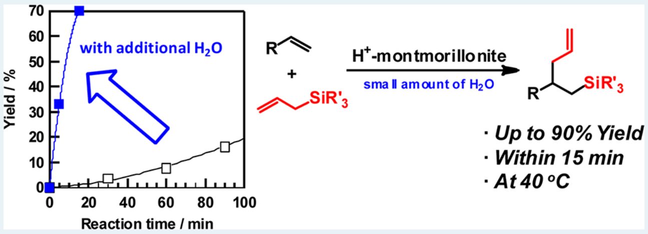
Water-Accelerated Allylsilylation of Alkenes Using a Proton-Exchanged Montmorillonite Catalyst

Ken Motokura, Shigekazu Matsunaga, Hiroto Noda, Akimitsu Miyaji, and Toshihide Baba*

Interdisciplinary Graduate School of Science and Engineering, Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 226-8502 Japan

Supporting Information

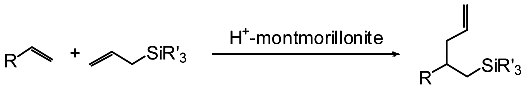
ABSTRACT: The addition of a small amount of water induced a dramatic accelerating effect on allylsilylation catalyzed by H^+-exchanged montmorillonite, enhancing the catalytic activity by greater than 60-fold. The allylsilylation of aromatic and aliphatic alkenes was completed within 15−60 min at 40 °C. It is possible that the active disilyl cation intermediate is stabilized by water molecules on the montmorillonite surface.



KEYWORDS: *allylsilylation, montmorillonite, water, alkene, allylsilane*

INTRODUCTION

Cation-exchanged montmorillonite has been found to be a highly active heterogeneous catalyst for various organic reactions.[1−6] Recently, our group demonstrated proton-exchanged montmorillonite (H^+-montmorillonite)-catalyzed allylsilylation of alkenes (eq 1).[7] A disilylpropyl cation formed through the reaction of two allylsilane molecules and a H^+ site was proposed as an active intermediate for the allylsilylation reaction.[7,8]



(1)

Montmorillonite naturally contains adsorbed water on its outer surface and in its interlayer space.[9,10] Collet and Laszlo reported the influence of water on the clay-catalyzed Diels−Alder reaction.[11] The stereoselectivity of the product depends on the amount of residual water of the clay. During the course of our investigation of 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. Herein, we report (i) the relationship between the amount of adsorbed and additional water and catalytic activity and (ii) the role of water in the catalytic allylsilylation reaction.

RESULTS AND DISCUSSION

H^+-montmorillonite was prepared from Na^+-montmorillonite using a previously reported ion exchange procedure with aqueous hydrogen chloride.[7,12,13] Physicochemical properties, such as acid amount (0.86 mmol/g), strength (ΔH = 111 kJ/mol), and concentration (6.3×10^{-3} mmol/m^2), of the H^+-montmorillonite was reported in other literature.[12,13] The prepared H^+-montmorillonite was stored under 30% humidity for at least 1 week.[14] To prepare H^+-montmorillonites with different amounts of adsorbed water, H^+-montmorillonite was dried under vacuum (~1 mm Hg) at 25, 100, and 120 °C for 1 h.

The amount of adsorbed water was determined by thermal gravimetric analysis (TGA). Figure 1A shows the TGA curves of H^+-montmorillonites with different amounts of adsorbed water. Aliouane and co-workers have reported that the two periods of weight loss, below 100 °C and between 100 and 150 °C, during TGA analysis are assignable to weakly linked water and H^+-coordinated water (H_3O^+), respectively.[10] On the basis of 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 1). 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 supports that the weight loss below 150 °C corresponds to adsorbed water.

Maintenance of the layered structure of H^+-montmorillonite after heat treatment was confirmed by X-ray diffraction (XRD) measurement. Figure 2 shows XRD spectra of H^+-montmorillonite treated at different temperatures. The interlayer distance of the H^+-montmorillonite was determined by subtracting the *c* dimension of the silicate sheet (9.6 Å) from the observed d_{001} values in the XRD spectrum. The interlayer distance values are summarized in Table 1; these were found to decrease as the amount of adsorbed water decreased.[10]

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 (eq 2).

Received: April 16, 2012
Revised: June 22, 2012
Published: August 8, 2012

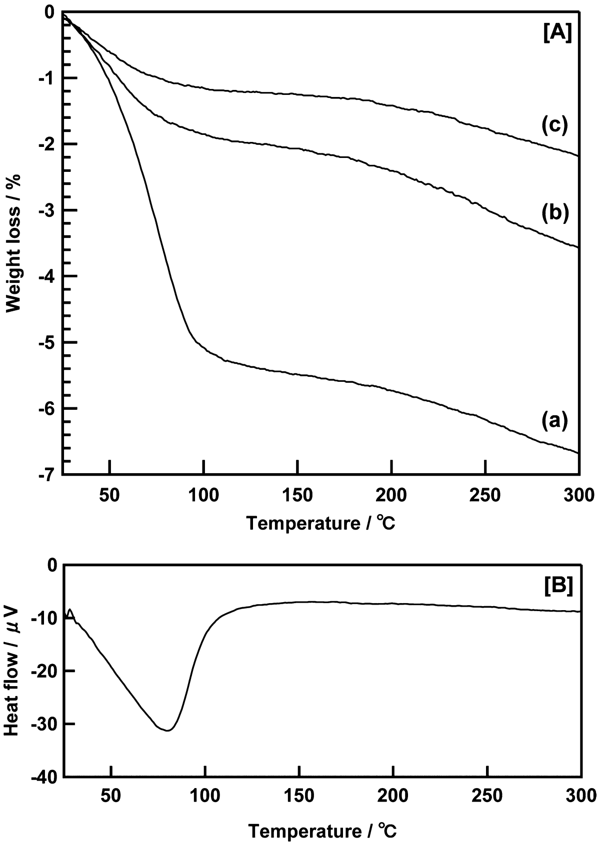
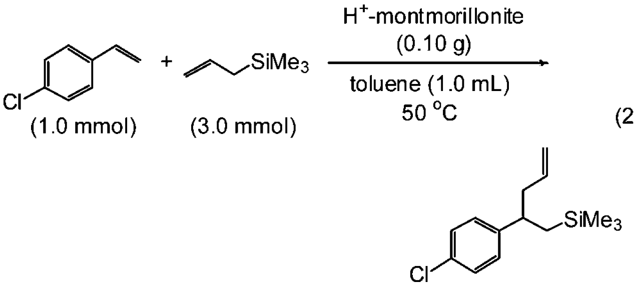


Figure 1. [A] Weight loss of (a) H^+-montmorillonite-(5.6), (b) H^+-montmorillonite-(2.1), and (c) H^+-montmorillonite-(1.3) versus temperature. [B] DTA curve of H^+-montmorillonite-(5.6).

Table 1. Properties 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 shown in Figure 2.



(2)

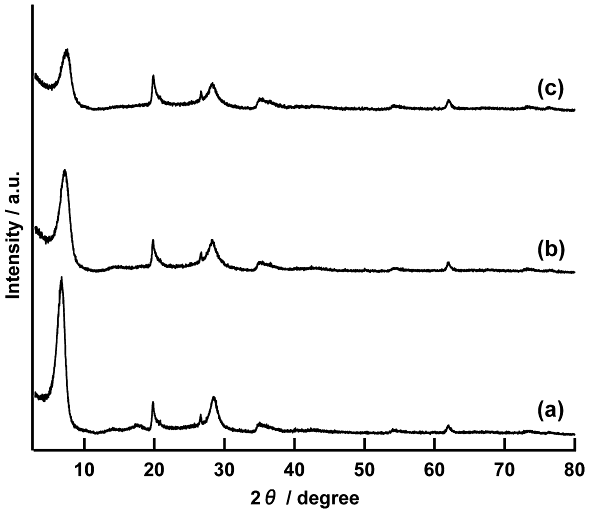


Figure 2. XRD spectra of (a) H^+-montmorillionite-(5.6), (b) H^+-montmorillionite-(2.1), and (c) H^+-montmorillionite-(1.3).

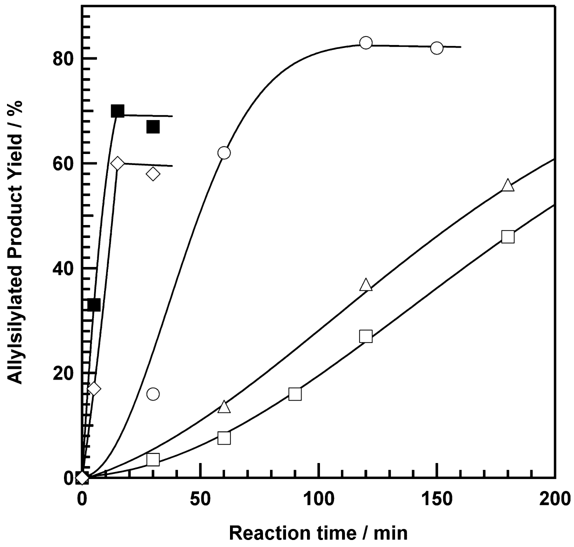
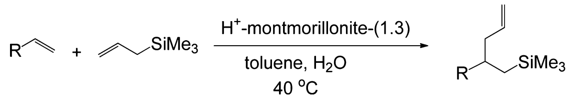


Figure 3. Time course for allylsilylation of *p*-chlorostyrene with allyltrimethylsilane using (□) H^+-montmorillonite-(1.3), (Δ) H^+-montmorillonite-(2.1), (○) H^+-montmorillonite-(5.6), (■) H^+-montmorillonite-(1.3) with 7.5 mg of H_2O, and (◊) H^+-montmorillonite-(1.3) with 10 mg of H_2O. Reaction conditions are shown in eq 2.

Figure 3 shows the time course of the product yield. Catalytic activity increased with the amount of adsorbed water (H^+-montmorillonite-(1.3) < -(2.1) < -(5.6)). Next, allylsilylation using H^+-montmorillonite-(1.3) was carried out in the presence of additional small amounts of 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 (■) compared with no additional water (□). A further increase in the reaction rate was not observed with the addition of 10 mg of water (◊). When the amount of water was increased to 50 mg, an induction period was observed in the allylsilylation (Figure 1S, Supporting Information). During the induction period, water was consumed by the reaction with allyltrimethylsilane to give hexamethyldisiloxane ($Me_3SiOSiMe_3$), then the allylsilylation started in the presence of the appropriate amount of water.

The allylsilylation of various alkenes was examined in the presence of additional H_2O, and the results are summarized in Table 2. The reaction of styrenes having an electron-withdrawing group proceeded at 40 °C. For example, the reaction of *p*-chlorostyrene was completed within 15 min, giving a 90% yield of the product, whereas a yield of only 2% was obtained in the absence of additional H_2O under the same reaction conditions. The reaction of styrene or 1-hexene with allyltrimethylsilane was also accelerated by additional H_2O.

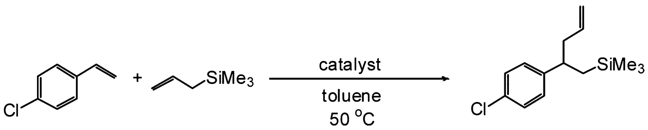
Table 2. H^+-Montmorillonite-Catalyzed Allylsilylation of Alkens with Allylsilane at 40 °C in the Presence of the Additional H_2O[a]



alkene (R=)	time (min)	conv. of alkene (%)[b]	yield (%)[b]
p-Cl-Ph–	15	93 (2)[c]	90 (2)[c]
p-F-Ph–	15	91	81
p-Br-Ph–	60	99	74
Ph–	15	95 (4)[c]	55 (2)[c]
n-C_4H_9–	15	96	64

[a] Reaction conditions: alkene (1.0 mmol), allylsilane (3.0 mmol), H^+-montmorillonite (0.10 g), toluene (1.0 mL), H_2O (7.5 mg), 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. Values in parentheses are product yield in the absence of H_2O. [b] Determined by GC and ^1H NMR using the internal standard technique. [c] Values in parentheses are conversion or yield in the absence of the additional H_2O.

Table 3. Allylsilylation of *p*-Chlorostyrene with Allyltrimethylsilane in the Presence and Absence of H_2O Using Various Acids[a]



catalysts and additives	conv. of allylsilane (%)[b]	conv. of styrene (%)[b]	yield (%)[b,c]
H^+-montmorillonite-(5.6)	72	99	83
montK10	26	12	11
montK10 + H_2O	11	3	<1
silica–alumina	33	<1	0
silica–alumina + H_2O	54	<1	0
amberlyst	83	9	trace
amberlyst + H_2O	>99	31	trace
p-toluenesulfonic acid	50	2	0
p-toluenesulfonic acid + H_2O	>99	1	0

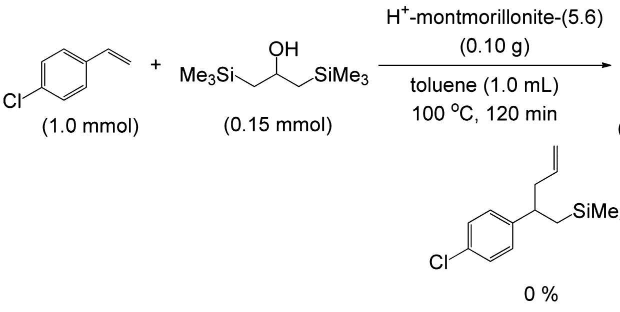
[a] Reaction conditions: *p*-chlorostyrene (1.0 mmol), allyltrimethylsilane (3.0 mmol), H^+-montmorillonite (0.10 g), toluene (1.0 mL), 50 °C, 120 min. [b] Determined by GC and ^1H NMR using internal standard technique. [c] Based on *p*-chlorostyrene used.

We have previously reported that allylsilylation hardly proceeded when other Brønsted acids were used instead of H^+-montmorillonite.[7] Because water had an accelerating effect on the reaction, allylsilylation using other Brønsted acids in the presence of H_2O was investigated. The results are shown in Table 3. The allylsilylated product hardly obtained, even in the presence of H_2O, with any other Brønsted acid but H^+-montmorillonite and commercially available montK10. However, for all these Brønsted acids, hydrolysis of allylsilane to silanol and disiloxane was enhanced by the addition of H_2O. These results indicate that allylsilylation is selectively accelerated by water on the montmorillonite surface compared with other acid catalysts. We also examined the allylsilylation using montK10, as shown in Table 3. The allylsilylated product yields were 11% and <1% in the absence and presence of H_2O, respectively. This is an inverse result from H^+-montmorillonite. The reason is unclear. However, it can be said that the character of the active site on the H^+-montmorillonite prepared from Na^+-montmorillonite and HCl aq. is different from commercially available montK10.

The interlayer space of montmorillonite expands slightly in nonpolar solvents.[15] However, this expanded interlayer space is not sufficient to allow the entrance and reaction of organic molecules. The allylsilylation reaction proceeded in toluene, a nonpolar solvent. As shown in Table 1, the interlayer distances of the H^+-montmorillonites (2.4–3.4 Å), which correspond to the size 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 do not affect their catalytic performances in the allylsilylation reaction.

To investigate the participation of silanol and disiloxane in the catalytic cycle, the reaction of *p*-chlorostyrene with allyltriethylsilane [allyl($SiEt_3$)] in the presence of either methoxytrimethylsilane ($MeOSiMe_3$)[16] or hexamethyldisiloxane ($Me_3SiOSiMe_3$) was carried out. No trimethylsilyl ($SiMe_3$) group was incorporated into the allylsilylation product in either case. Thus, the possibility that silanol and disiloxane act as precursors of the catalytically active intermediate can be excluded.

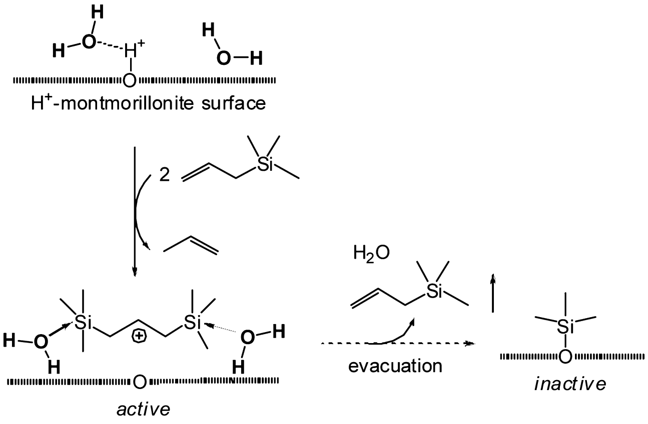
We previously reported that the catalytically active species for allylsilylation is a disilylpropyl cation formed in the reaction between allylsilane and the H^+ site of H^+-montmorillonite.[7] This is supported by the following results. The reaction of allyltriethylsilane with 1,3-bis(trimethylsilyl)-2-propanol affords an allylsilylation product containing the $SiMe_3$ group.[7] The reaction between styrene and 1,3-bis(trimethylsilyl)-2-propanol in the absence of allyltrimethylsilane did not afford allylsilylated product at all (eq 3). This result clearly indicates that the disilyl cation is a source of the only silyl group of the allylsilylated styrene.[17] Solid-state ^{13}C and ^{29}Si NMR studies revealed that the disilylpropyl cation decomposed easily to the inactive monomeric $SiMe_3$ species after evacuation of excess allyltrimethylsilane.[7]



(3)

The proposed decomposition pathway is shown in Scheme 1. One possible explanation of the role of water is stabilization of the active disilyl cation on the montmorillonite surface or edges via electron donation from water molecules, as shown Scheme 1. To investigate the interaction between the Si group and the water molecule, the reaction using allyltri*ethyl*silane was examined in the presence and absence of additional H_2O at 40 °C, as shown in Scheme 2. The reaction of *p*-chlorostyrene with allyltriethylsilane was accelerated by the additional H_2O; however, the accelerating effect was much smaller than the reaction of allyltrimethylsilane.[18] Because of the bulky ethyl group on the Si atom, the interaction between the $SiEt_3$ group

Scheme 1. Proposed Electron-Donating Stabilization of the Active Disilyl Cation by Water Molecules and Reaction Pathways for the Formation and Decomposition of the Disilyl Cation

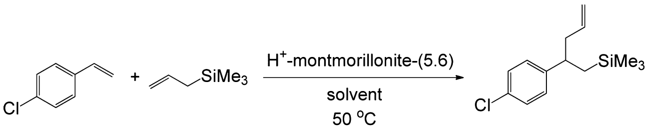


and the H_2O molecule is much weaker compared with the $SiMe_3$ group. This result suggests that the interaction between the Si atom and the H_2O molecule (Scheme 1) plays a key role for the acceleration of the allylsilylation.

If the carbocation center is more electrophilic than the silyl group of the disilyl cation, 1,3-bis(trimethylsilyl)-2-propanol should form in the presence of H_2O. We carefully checked the reaction mixture; however, 1,3-bis(trimethylsilyl)-2-propanol was not detected. This result indicates that the Si center is more electrophilic in the disilyl cation. Because the Si atom shows a high affinity for the oxygen atom, the H_2O molecule might have an interaction with the Si atom of the cationic species (Scheme 1). Formation of silanol as a byproduct also supports this hypothesis.

The allylsilylation with nonpolar, polar protic, and polar aprotic solvents using H^+-montmorillonite with residual water was examined, as shown in Table 4. The allylsilylation proceeded effectively with nonpolar and water-insoluble solvents, such as dichloromethane. Laszlo et al. also reported a Diels–Alder reaction using the clay catalyst with residual water in dichloromethane solvent.[11] On the other hand, the product was hardly obtained in the case of water-soluble solvents, such as 1,4-dioxane and DMF. Two reasons for the significantly low catalytic performances are expected: (i) adsorption of the polar solvent to the active acid site and (ii) removal of H_2O molecules from the montmorillonite surface to the solvent. The presence of the water molecule close to the active site on the montmorillonite is highly important.

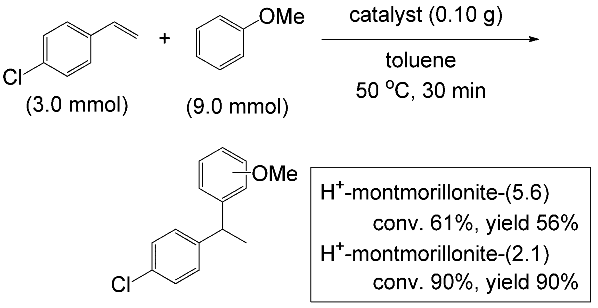
Table 4. Solvent Effect on the Allylsilylation of *p*-Chlorostyrene with Allyltrimethylsilane Using H^+-Montmorillonite[a]



solvent	conv. of allylsilane (%)[b]	conv. of styrene (%)[b]	yield (%)[b,c]
toluene	72	99	83
dichloromethane[d]	99	>99	82
n-heptane	64	87	61
1,4-dioxane	34	5	1
DMF[e]	15	5	<1
DMSO[f]	6	<1	<1
methanol	22	2	<1

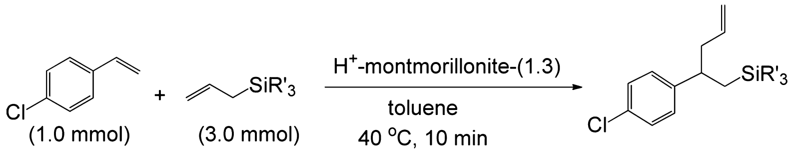
[a] Reaction conditions: *p*-chlorostyrene (1.0 mmol), allyltrimethylsilane (3.0 mmol), H^+-montmorillonite-(5.6) (0.10 g), solvent (1.0 mL), 50 °C, 120 min. [b] Determined by GC and ^1H NMR using internal standard technique. [c] Based on *p*-chlorostyrene used. [d] 40 °C. [e] *N*,*N*-Dimethylformamide. [f] Dimethyl sulfoxide.

To investigate the effect of water on other acid-catalyzed reactions, Friedel–Crafts alkylation of anisole with *p*-chlorostyrene was examined using H^+-montmorillonite with different amounts of adsorbed water. As shown in eq 4, H^+-montmorillonite-(2.1) showed higher catalytic activity than H^+-montmorillonite-(5.6). Friedel–Crafts alkylation using H^+-montmorillonite was not accelerated by adsorbed water. The alkylation reaction is initiated by protonation of the carbon–carbon double bond of styrene. In contrast, the allylsilylation of alkenes is initiated by the formation of a cationic Si species in the reaction between H^+ and allylsilane. This result supports that water participates by acceleration of a catalytic reaction, including formation of cationic Si species.



(4)

Scheme 2. Allylsilylation of *p*-Chlorostyrene with Allyltrimethylsilane or Allyltriethylsilane in the Presence and Absence of Additional H_2O



	Yield (%)	
	with H_2O	without H_2O
R'=Me	73	<1
R'=Et	8	<1

SUMMARY

In summary, the accelerating effect of water on the allylsilylation of alkenes was discovered. The reaction rate in the initial period was increased by a factor of 60 by the addition of a small and optimal amount of water. Among the various Brønsted acids examined, only H^+-montmorillonite showed such an accelerating effect. It is possible that the role of water in the allylsilylation reaction is to stabilize the catalytically active cationic Si species. The solvent effect also indicates the presence of a water molecule close to the active site is necessary for the acceleration of allylsilylation.

ASSOCIATED CONTENT

Supporting Information

Experimental details and time course for the reaction with 50 mg of water. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: tbaba@chemenv.titech.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Young Scientists (A) (24686092).

REFERENCES

(1) For Montmorillonite-catalyzed organic synthesis, see references 1−6. Kaneda, K. *Synlett* **2007**, 999.

(2) Kaneda, K.; Ebitani, K.; Mizugaki, T.; Mori, K. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 981.

(3) Izumi, Y.; Urabe, K.; Onaka, M. *Microporous Mesoporous Mater.* **1998**, *21*, 227.

(4) Clark, J. H.; Macquarrie, D. J. *Chem. Soc. Rev.* **1996**, *25*, 303.

(5) Izumi, Y.; Onaka, M. *Adv. Catal.* **1992**, *38*, 245.

(6) Laszlo, P. *Acc. Chem. Res.* **1986**, *19*, 121.

(7) Motokura, K.; Matsunaga, S.; Miyaji, A.; Sakamoto, Y.; Baba, T. *Org. Lett.* **2010**, *12*, 1508.

(8) Motokura, K.; Baba, T. *Green . Chem.* **2012**, *14*, 565.

(9) Bergaya, F.; Theng, B. K. G.; Lagaly, G., Eds.; *Handbook of Clay Science*, Elsevier Science: Amsterdam, 2006.

(10) Aliouane, N.; Hammouche, A.; De Doncker, R. W.; Telli, L.; Boutahala, M.; Brahimi, B. *Solid State Ionics* **2002**, *148*, 103.

(11) Collet, C.; Laszlo, P. *Tetrahedron Lett.* **1991**, *32*, 2905.

(12) Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2605.

(13) Motokura, K.; Nakagiri, N.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **2007**, *72*, 6006.

(14) Stable values of adsorbed water in H^+-montmorillonite are achieved only after 2−5 days at the same level of humidity due to the slow hydration process. See ref 10.

(15) A slight expansion of the interlayer space of wet montmorillonite with toluene was observed by XRD analysis.

(16) Methoxytrimethylsilane is easily decomposed by adsorbed H_2O to form trimethylsilanol.

(17) We examined the reaction between 1,3-bis(trimethylsilyl)-2-propanol and allyltriethylsilane. The exchange of the silyl group was observed. This result supports that (i) the disilyl cation can activate the C−C double bond and (ii) the disilyl cation acts as a reservoir of the allylsilane, preventing the decomposition and formation of inactive monomeric Si species.

(18) The reactivity of allyltriethylsilane was not so different compared with the allyltrimethylsilane without additional water at 100 °C. See reference 7.

NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on August 13, 2012, with incorrect artwork for equation 4. The corrected version was reposted on August 17.