Catal Lett (2008) 123:72–79
DOI 10.1007/s10562-008-9395-7

Vapor-phase Hydrosilylation Using a Transition Metal Complex Catalyst in a Liquid Polymer Medium Supported on Silica Gel

Masaki Okamoto · Hironari Kiya · Akihiko Matsumura · Eiichi Suzuki

Received: 10 October 2007 / Accepted: 4 January 2008 / Published online: 23 January 2008

Abstract Transition metal catalysts in various liquid polymer media supported on silica gel were prepared and used for vapor-phase hydrosilylation. Tetraammineplatinum(II) chloride and potassium hexachloroplatinate(IV) in a polyethylene glycol (PEG) medium showed high and stable activity. Deactivation of the catalyst was not observed unless a high platinum concentration in PEG was used. When the amount of PEG was 40 vol% of the pore volume of silica gel, PEG was coated on the pore walls of the silica gel, and did not block the pore openings. Active species in the PEG were formed only during the reaction.

Keywords Hydrosilylation · Platinum catalyst · Polyethylene glycol · Supported liquid phase catalyst

1 Introduction

Hydrosilylation leads to the formation of silicon–carbon bonds, and is one of the most important reactions in the synthesis of organosilanes. For example, acetylene reacts with trichlorosilane to afford vinyltrichlorosilane, which is synthesized industrially and used as a silane-coupling reagent. In general, hydrosilylation is performed in the liquid phase using a platinum complex such as hexachloroplatinum(IV) acid [1–3]. However, there are drawbacks to this method, such as the difficulty of separating the catalyst from the reaction mixture. A vapor flow system using a solid catalyst is a solution to these problems.

In our previous report [4], a tetraammineplatinum(II) chloride catalyst in a polyethylene glycol (PEG) medium supported on silica gel ($Pt(NH_3)_4Cl_2$–PEG/SiO_2) was shown to be very active and stable for vapor-phase hydrosilylation of acetylene with trichlorosilane and trimethoxysilane. This catalyst is an example of supported liquid-phase catalysts (SLPCs) [5–13]. In general, a SLPC is a homogeneous catalyst dissolved in a solvent with a high boiling point or molten salt distributed in pores of porous support. Thus, a SLPC has the properties of both homogenous and heterogeneous catalysts. In our unique SLPC, a polymer was used as a liquid phase; i.e., the platinum complex was dissolved in a liquid polymer, allowing the catalyst to be handled as a solid. Because PEG, the polymer we used as a liquid polymer, has very low vapor pressure at high temperatures, and is stable, non-toxic, inexpensive, and readily available, it is a suitable candidate for a SLPC solvent. Furthermore, in hydrosilylation of acetylene, a platinum metal catalyst, which is a typical solid catalyst for hydrosilylation, was deactivated because of strong adsorption of acetylene on the metal surface [4, 14], whereas the platinum complex-PEG catalyst supported on silica has tolerance for acetylene.

In this work, various transition metal complex catalysts in several polymer media supported on silica gels were prepared and used for vapor-phase hydrosilylation. Moreover, the effects of reaction variables were examined, and the catalysts were characterized by nitrogen adsorption, temperature-programmed desorption (TPD), and extended X-ray absorption fine structure (EXAFS) to explain their high activity.

M. Okamoto (✉)
Department of Applied Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan
e-mail: mokamoto@apc.titech.ac.jp

H. Kiya · A. Matsumura · E. Suzuki
Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8550, Japan

2 Experimental

2.1 Catalyst Preparation

A typical catalyst was prepared as follows: Silica gel, Micro Bead 300A (surface area 128 m^2 g^{-1}, pore volume, 1.17 mL g^{-1}; average pore diameter, 27.5 nm) obtained from Fuji Silysia Chemical Ltd., was dried at 170 °C for 24 h in an oven. Tetraammineplatinum(II) chloride ($Pt(NH_3)_4Cl_2{\cdot}H_2O$, Strem Chemicals, 19.4 mg) was dissolved in a mixture of 1.15 g of PEG (average molecular weight: 1,000, Kanto Chemical Co.) and 8 mL of water, and then 2.15 g of silica gel was added to the solution. The mixture was allowed to settle for 24 h and was then dried using a rotary evaporator to obtain the $Pt(NH_3)_4Cl_2$–PEG/SiO_2 catalyst. The amount of Pt catalyst obtained was 0.5 wt% of the silica gel, and the amount of PEG was 40 vol% of the pore volume of the silica gel. When poly(aminopropylmethyl)siloxane (Dow Corning Toray Co.) and polyethylene (Aldrich) were used as a polymer, acetone was used to dissolve them.

2.2 Reaction Procedure

The catalyst (300 mg) was placed in a reactor tube (quartz; i.d., 10 mm) of a fixed-bed flow reactor system. The catalyst was pretreated at 150 °C for 1 h in a helium stream, prior to the reaction of acetylene (76 kPa) with trichlorosilane (19 kPa) at 150 °C. The products were identified by GC–MS and analyzed by gas chromatography. Yields of hydrosilylation products were calculated based on trichlorosilane.

2.3 Catalyst Characterization

Nitrogen adsorption measurement was performed with Bellsorp. Prior to the measurement, the catalyst was kept under vacuum at 150 °C for 5 h. The pore size distributions were calculated using desorption isotherms. TPD profiles were obtained using a vacuum system equipped with a quadrupole mass spectrometer. The catalysts were pretreated at 100 °C for 2 h and then cooled to room temperature. The TPD measurement started at room temperature and proceeded to 220 °C at a rate of 5 °C min^{-1}. EXAFS analysis was performed at the BL-7C facility of the Photon Factory at the High Energy Accelerator Research Organization, Japan. Pt L_{III}-edge absorption spectra were recorded in fluorescence mode at 295 K.

3 Results and Discussion

3.1 Hydrosilylation of Acetylene with Trichlorosilane

3.1.1 *Various Transition Metal Catalysts in PEG Supported on Silica*

Various transition metal complexes and PEG as a liquid phase were used for preparation of the catalyst for hydrosilylation. The reaction results are summarized in Table 1. Supported platinum metal catalysts, Pt/SiO_2 and Pt/Al_2O_3, were deactivated significantly and showed very low activities after 6 h on stream. On the other hand, $Pt(NH_3)_4Cl_2$–PEG/SiO_2 and K_2PtCl_6–PEG/SiO_2 showed high activities, and double hydrosilylation proceeding to form bis(trichlorosilyl)ethane (Scheme 1) was also observed. When hexachloroplatinum(IV) acid, the most common catalyst for liquid-phase hydrosilylation, was loaded with PEG on silica gel, the reaction did not proceed after 6 h. EXAFS analysis revealed that the hexachloroplatinum(IV) acid was completely reduced to platinum metal during the reaction, which explains the deactivation of the catalyst and the lack of hydrosilylation activity after 6 h. The complexes of other metals, such as rhodium, palladium, ruthenium, and nickel, which are known to catalyze hydrosilylation in a liquid phase, were also used to form the hydrosilylation catalysts. However, they showed no or very low activity with the exception of for rhodium(III) chloride, which is less active than the platinum complexes.

$$\mathrm{HC{\equiv}CH} \xrightarrow{+\ \mathrm{HSiX_3}} \mathrm{H_2C{=}CHSiX_3} \xrightarrow{+\ \mathrm{HSiX_3}} \mathrm{X_3SiH_2C{-}CH_2SiX_3}$$

Scheme 1 Formation of bis(trichlorosilyl)ethane

3.1.2 *Platinum Catalysts in Various Polymer Media Supported on Silica*

Table 2 shows the results of hydrosilylation using platinum complexes in various polymer media supported on silica as catalysts. When a shorter PEG (with an average molecular weight of 400) was used, the results did not change, indicating that polymer length does not affect the activity. However, since a shorter polymer has a higher vapor pressure at the reaction temperature [15], low molecular weight PEG tends to evaporate during the reaction and was deposited on the wall of reactor below the catalyst bed. In the case of PEG with an average molecular weight of 1,000, the amount of PEG evaporated after 6 h under reaction conditions is estimated to be 0.01% based on vapor pressure data [15]. The catalyst

Table 1 Hydrosilylation of acetylene with trichlorosilane using various metal complexes dissolved in a PEG supported on silica gel

Catalyst	Trichlorosilane conversion (%)	Yield (%)		
		$C_2H_3SiCl_3$	$Cl_3SiC_2H_4SiCl_3$	$SiCl_4$
$Pt(NH_3)_4Cl_2$–PEG/SiO_2[a]	84	72	2	6
K_2PtCl_6–PEG/SiO_2[a]	83	67	7	6
K_2PtCl_4–PEG/SiO_2[a]	35	30	2	2
H_2PtCl_6–PEG/SiO_2	0	0	0	0
$PtCl_4$–PEG/SiO_2	0	0	0	0
$Pt(acac)_2$–PEG/SiO_2	53	46	2	3
$Pt(NH_3)_4Cl_2/SiO_2$	38	35	0	2
Pt/SiO_2	0	0	0	0
Pt/Al_2O_3	4	2	0	1
$RhCl_3$–PEG/SiO_2	40	38	0	1
$Rh(OAc)_2$–PEG/SiO_2	0	0	0	0
$Pd(NH_3)_4Cl_2$–PEG/SiO_2	5	2	0	2
$RuCl_3$–PEG/SiO_2	0	0	0	0
$Ru(acac)_3$–PEG/SiO_2	0	0	0	0
$Ni(acac)_2$–PEG/SiO_2	0	0	0	0

[a] Data from Ref. [4]

The metal content was 0.5 wt%. PEG volume was 40 vol% of the pore volume of silica gel. The reaction was carried out at 150 °C at 19 kPa of $HSiCl_3$ and 76 kPa of C_2H_2 using 300 mg of the catalyst. The contact time, *W*/*F*, was 19 g h mol^{-1}. The results were obtained after 6 h of time on stream

Table 2 Hydrosilylation of acetylene with trichlorosilane using $Pt(NH_3)_4Cl_2$ dissolved in various media supported on silica gel

Catalyst	Trichlorosilane conversion (%)	Yield (%)		
		$C_2H_3SiCl_3$	$Cl_3SiC_2H_4SiCl_3$	$SiCl_4$
$Pt(NH_3)_4Cl_2$–PEG/SiO_2	84	72	2	6
$Pt(NH_3)_4Cl_2$–PEG(400)/SiO_2[a]	82	71	2	6
$Pt(NH_3)_4Cl_2$–PAPMS/SiO_2[b]	0	–	–	–
$Pt(acac)_2$–PE/SiO_2[c]	10	8	0	1
$Pt(NH_3)_4Cl_2$–EMICl/SiO_2[d]	0	–	–	–

[a] PEG(400): polyethylene glycol (average molecular weight: 400)

[b] PAPMS: poly(aminopropylmethyl)siloxane (average molecular weight: 2,800)

[c] PE: polyethylene (average molecular weight: 4,000)

[d] EMICl: 1-ethyl-3-methylimidazolium chloride

The platinum content was 0.5 wt%. The medium volume was 40 vol% of the pore volume of silica gel. The reaction was carried out at 150 °C at 19 kPa of $HSiCl_3$ and 76 kPa of C_2H_2 using 300 mg of the catalyst. The contact time, *W*/*F*, was 19 g h mol^{-1}. The results were obtained after 6 h of time on stream

using polysiloxane containing an amino group, which can be coordinated to platinum, showed no activity. Use of polyethylene (PE) with $Pt(acac)_2$ resulted in deactivation of the catalyst and low yield of vinyltrichlorosilane. PE cannot be coordinated to Pt. This probably causes deactivation due to Pt reduction. 1-Ethyl-3-methylimidazolium chloride (EMICl), which is an ionic liquid, was also unsuitable as a liquid medium, as the color of the catalyst used did not darken, which shows that Pt was not reduced to metal. When EMICl was used, it is possible that EMI ion is coordinated to Pt to form a catalytically non-active Pt complex, which leads to no reaction. In conclusion, a combination of $Pt(NH_3)_4Cl_2$ and a longer PEG resulted in the optimal catalyst for hydrosilylation of acetylene, because of high and stable activity and no loss of PEG.

3.1.3 Effects of Platinum Content and PEG Volume

The platinum content and PEG volume load were varied to prepare several catalysts. As shown in Table 3, trichlorosilane conversion increased with an increase in platinum content. However, use of 1.0 wt% of platinum resulted in a decrease of vinyltrichlorosilane yield because of double

Table 3 Effects of platinum content and PEG volume loaded on hydrosilylation of acetylene with trichlorosilane

Pt (wt%)	PEG (vol%)	Trichlorosilane conversion (%)		Vinyltrichlorosilane yield (%)	
		2 h[a]	6 h[a]	2 h[a]	6 h[a]
0.25	40	74	74	67	68
0.5	40	84	84	71	72
1.0	40	98	84	62	66
0.5	20	97	76	75	66
0.5	80	64	65	58	58

[a] The results were obtained after 2 and 6 h of time on stream

The reaction was carried out at 150 °C at 19 kPa of $HSiCl_3$ and 76 kPa of C_2H_2 using 300 mg of the catalyst. The contact time, *W*/*F*, was 19 g h mol^{-1}

hydrosilylation to afford bis(trichlorosilyl)ethane. Increasing the PEG volume decreased catalytic activity. Because hydrosilylation proceeded in a PEG liquid film on the surface of these catalysts, a low platinum concentration in PEG, i.e., a large volume of PEG, led to low activity. When the platinum concentration in PEG was high, trichlorosilane conversion decreased with increase of time on stream. EXAFS measurements of catalysts with high platinum concentration indicated that platinum was reduced to metal. Indeed, a high platinum concentration brought about the reduction of platinum, and consequently the catalyst was deactivated.

3.1.4 *Effects on Reaction Conditions*

The effects on reaction temperature, contact time, and the ratio of acetylene to trichlorosilane, were examined.

The reaction temperature was varied from 130 to 200 °C. Figure 1 shows how the reaction proceeds as a function of time on stream. Increasing the temperature to 150 °C increased vinyltrichlorosilane yield. At the beginning of the reaction, the yield increased with time, indicating the presence of active species during the reaction. At 170 °C, the yield was higher but decreased to below 50% as time on stream increased. Raising the temperature to 200 °C led to a low yield of about 30%. The highest catalytic performance was observed at 150 °C, and the color of the catalyst used at a higher temperature was dark grey. This strongly suggests that at a higher temperature, the platinum complex in the catalyst was decomposed by heat to produce platinum metal, which is less active for hydrosilylation.

Figure 2 shows the effect of the molar ratio of acetylene to trichlorosilane. The partial pressure of trichlorosilane was kept constant at 19 kPa, and the acetylene pressure was varied. An increase in the acetylene pressure caused a slight increase of vinyltrichlorosilane yield and a decrease of the double hydrosilylation product, i.e., an excess amount of acetylene gave a high yield of vinyltrichlorosilane with high selectivity. Because acetylene reacts more readily with trichlorosilane than with vinyltrichlorosilane, double hydrosilylation was inhibited at a higher acetylene pressure. A slight disproportionation of trichlorosilane proceeded to form tetrachlorosilane and silane, and it was observed to be independent of the ratio of acetylene to trichlorosilane.

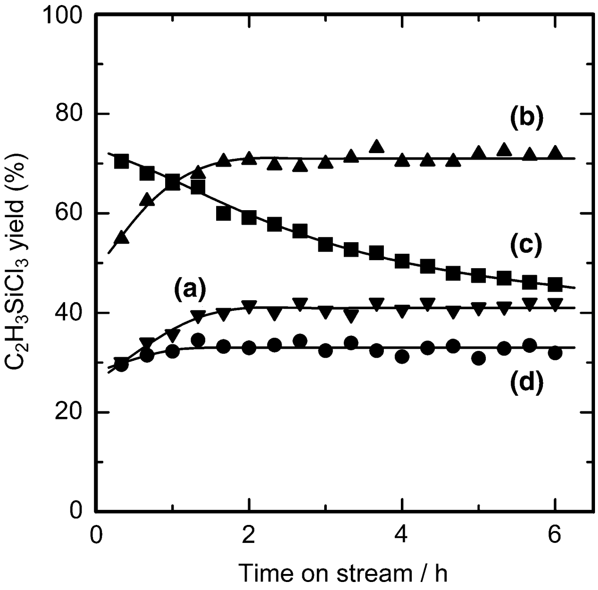

Fig. 1 Time evolution of vinyltrichlorosilane yield during the reaction of acetylene with trichlorosilane at 130 °C (**a**), 150 °C (**b**), 170 °C (**c**), and 200 °C (**d**). The platinum content was 0.5 wt%. PEG volume was 40 vol% of the pore volume of silica gel. The reaction was carried out at 19 kPa of $HSiCl_3$ and 76 kPa of C_2H_2 using 300 mg of the catalyst. The contact time, *W*/*F*, was 19 g h mol^{-1}

Contact time also affected the vinyltrichlorosilane and 1,2-bis(trichlorosilyl)ethane yields as shown in Fig. 3. Longer contact time led to a higher yield of the double hydrosilylation product as well as vinyltrichlorosilane, because the primary product, vinyltrichlorosilane, was in contact with the catalyst for a long time. The yield of tetrachlorosilane formed by disproportionation of trichlorosilane was not changed with contact time.

3.2 Hydrosilylation with Trimethoxysilane

The $Pt(NH_3)_4Cl_2$–PEG/SiO_2 catalyst also showed high activity for hydrosilylation of acetylene with trimethoxysilane instead of trichlorosilane [4]. Figure 4 shows time evolution of vinyltrimethoxysilane yield at various reaction temperatures. At the beginning, the yield increased slightly and then became constant at 130 and 150 °C, as shown in Fig. 1. This is similar to the time evolution of

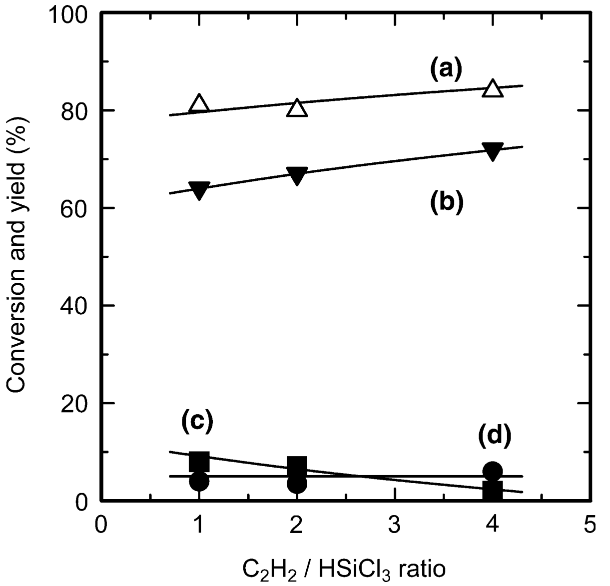

Fig. 2 Effect of molar ratio of acetylene to trichlorosilane on trichlorosilane conversion (**a**), vinyltrichlorosilane yield (**b**), 1,2-bis(trichlorosilyl)ethane yield (**c**), and tetrachlorosilane yield (**d**). The amount of platinum content was 0.5 wt%. PEG volume was 40 vol% of the pore volume of silica gel. The reaction was carried out at 150 °C at 19 kPa of $HSiCl_3$ using 300 mg of the catalyst. The contact time, *W*/*F*, was 19 g h mol^{-1}

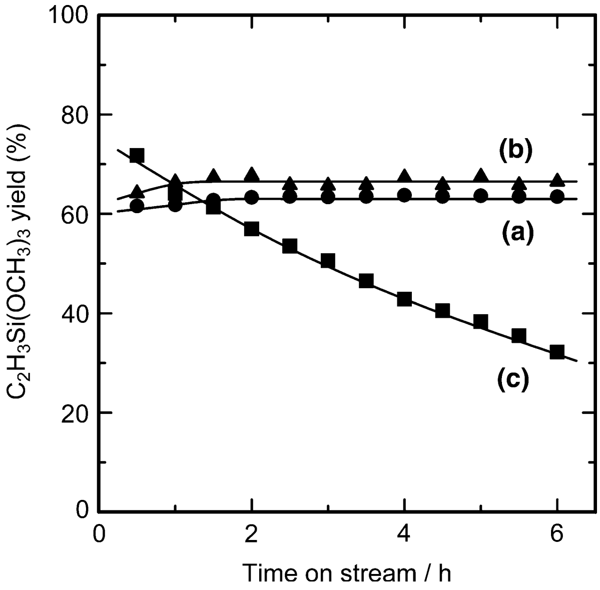

Fig. 4 Time evolution of the vinyltrimethoxysilane yield during the reaction of acetylene with trimethoxysilane at 130 °C (**a**), 150 °C (**b**), and 170 °C (**c**). The platinum content was 0.5 wt%. PEG volume was 40 vol% of the pore volume of silica gel. The reaction was carried out at 11 kPa of $HSi(OCH_3)_3$ and 44 kPa of C_2H_2 using 300 mg of the catalyst. The contact time, *W*/*F*, was 14 g h mol^{-1}

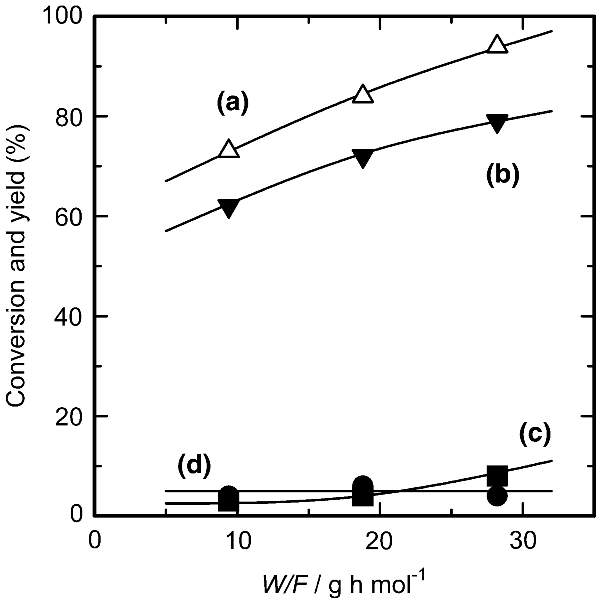

Fig. 3 Effect of contact time on trichlorosilane conversion (**a**), vinyltrichlorosilane yield (**b**), 1,2-bis(trichlorosilyl)ethane yield (**c**), and tetrachlorosilane yield (**d**). The platinum content was 0.5 wt%. PEG volume was 40 vol% of the pore volume of silica gel. The reaction was carried out at 150 °C at 19 kPa of $HSiCl_3$ and 76 kPa of C_2H_2 using 300 mg of the catalyst

hydrosilylation with trichlorosilane. At 170 °C, the yield decreased gradually, probably because of reduction of platinum complex. The double hydrosilylated product, 1,2-bis(trimethoxysilyl)ethane, was not formed at any temperatures.

Hydrosilylation of alkenes, ethylene and propylene with trimethoxysilane, was carried out using $Pt(NH_3)_4Cl_2$–PEG/SiO_2 as catalyst. As shown in Table 4, the trimethoxysilane conversion and the yield of hydrosilylated products were much lower than those obtained using acetylene. As reported earlier [4], in hydrosilylation with trichlorosilane the product yields were high using ethylene and propylene as well as acetylene. Using trimethoxysilane, a $Pt(NH_3)_4Cl_2$–PEG/SiO_2 catalyst was suitable only for alkyne hydrosilylation. The hydrosilylation of acetylene with trimethoxysilane did not yield 1,2-bis(trimethoxysilyl)ethane formed by hydrosilylation of vinyltrimethoxysilane. This is consistent with the low reactivity of the carbon–carbon double bond between ethylene (or propylene) and trimethoxysilane.

The hydrosilylations of acetylene with trichlorosilane and trimethoxysilane were carried out under same reaction conditions to compare their reactivity with the $Pt(NH_3)_4Cl_2$–PEG/SiO_2 catalyst. Trimethoxysilane was more reactive than trichlorosilane for the reaction with acetylene, as shown in Table 4. The reactivities of trichlorosilane and trialkoxysilane are dependent on the type of catalyst, and the reactivity using hexachloroplatinum(IV) acid as a catalyst was different from that using $Pt(NH_3)_4Cl_2$–PEG/SiO_2 [16]. Thus, this catalyst is suitable for hydrosilylation of alkyne with trialkoxysilane.

Table 4 Hydrosilylation of unsaturated hydrocarbons with trimethoxysilane and trichlorosilane over $Pt(NH_3)_4Cl_2$–PEG/SiO_2

Alkene and alkyne	X: $HSiX_3$	$HSiX_3$ conversion (%)	Yield (%) Hydrosilylated product
C_2H_4	OCH_3	8	5 $C_2H_5Si(OCH_3)_3$
C_3H_6	OCH_3	6	2 n-$C_3H_7Si(OCH_3)_3$
C_2H_2	OCH_3	70[a]	67[a] $C_2H_3Si(OCH_3)_3$
C_2H_2	Cl	61	52 $C_2H_3SiCl_3$

[a] Data from Ref. [4]

The reaction was carried out at 150 °C at 11 kPa of $HSiX_3$ and 44 kPa of unsaturated hydrocarbon using 300 mg of the catalyst. The contact time, *W*/*F*, was 14 g h mol^{-1}. The results were obtained after 6 h of time on stream

3.3 Characterization of the $Pt(NH_3)_4Cl_2$–PEG/SiO_2 Catalyst

The $Pt(NH_3)_4Cl_2$–PEG/SiO_2 catalyst was one of the best heterogeneous catalysts for the vapor-phase hydrosilylation as described above. This catalyst was characterized using nitrogen adsorption–desorption, temperature programmed desorption, and X-ray absorption fine structure.

3.3.1 Nitrogen Adsorption of As-made $Pt(NH_3)_4Cl_2$–PEG/SiO_2 Catalyst

Figure 5 shows the pore size distribution of SiO_2 and $Pt(NH_3)_4Cl_2$–PEG/SiO_2. Before the nitrogen adsorption–desorption measurement, $Pt(NH_3)_4Cl_2$–PEG/SiO_2 is evacuated at 150 °C for 5 h. After impregnating the PEG with the platinum complex, 45% of the pore volume of silica decreased. This value corresponds to volume of loaded PEG, indicating that the PEG does not block pore openings and pores remain after the PEG is impregnated with the platinum complex. Thus, a large area interface between the PEG liquid and gas phases was formed, and provided easy access for the reactants to reach the active species.

As shown in Table 3, the catalyst activity of 0.25 wt% Pt–40 vol% PEG catalyst was higher than that of 0.5 wt% Pt–80 vol% PEG catalyst. The Pt concentrations in the PEG of these catalysts were same, whereas the BET surface areas of the catalysts with 20 and 40 wt% of PEG were 22 and 64 m^2 g^{-1}, respectively. This also indicates that a large portion of the interface is required for high activity.

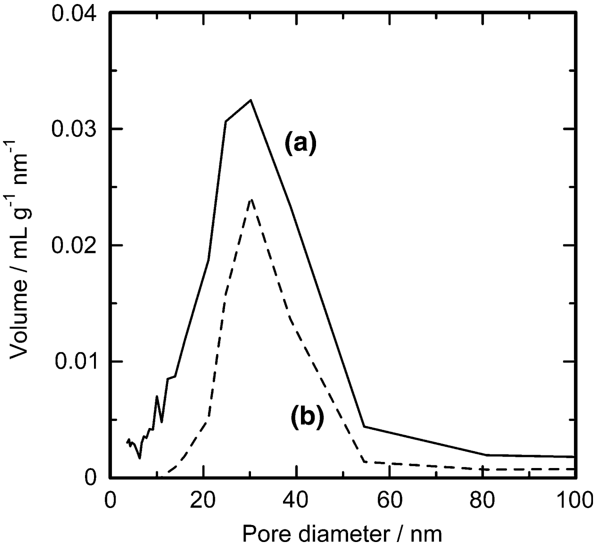

Fig. 5 Pore size distribution of SiO_2 (**a**) and $Pt(NH_3)_4Cl_2$–PEG/SiO_2 (**b**). The platinum content was 0.5 wt%. PEG volume was 40 vol% of the pore volume of silica gel

3.3.2 Temperature Programmed Desorption (TPD) Analysis of the $Pt(NH_3)_4Cl_2$–PEG/SiO_2 Catalyst

EXAFS analysis revealed that the ammine ligand is eliminated from $Pt(NH_3)_4Cl_2$–PEG/SiO_2 during pretreatment at 150 °C [4]. However, in general, $Pt(NH_3)_4Cl_2$ is decomposed at about 200 °C to form $Pt(NH_3)_2Cl_2$ [17]. To examine the changes in the catalyst, temperature programmed desorption (TPD) analysis of $Pt(NH_3)_4Cl_2$ and $Pt(NH_3)_4Cl_2$–PEG/SiO_2 was performed. Figure 6a shows the results of the platinum complex. Two peaks of mass number (*m*/*z*) 16 and 17 due to ammonia were observed around 190 °C. The TPD profile of the $Pt(NH_3)_4Cl_2$–PEG/SiO_2 catalyst is shown in Fig. 6b. Here, we see the peaks of 16 and 17 (*m*/*z*) due to ammonia, but the maximum temperature dropped to 180 °C and the peak widths broadened. This indicates that the ammine ligand of $Pt(NH_3)_4Cl_2$ in PEG is more readily eliminated than that in pure $Pt(NH_3)_4Cl_2$; i.e., the environment of $Pt(NH_3)_4Cl_2$ in PEG is different from that of pure $Pt(NH_3)_4Cl_2$.

Shoulder peaks were observed around 135 °C in both the 16 and 17 (*m*/*z*) profiles. The peak of the 18 (*m*/*z*) profile also appeared at the same temperature in the TPD profile of the catalyst. This peak is due to water, and the temperature of the maximum peak was almost the same as those of the two shoulder peaks. Because the mass numbers of fragment water ions are 17 and 16, the two shoulder peaks are probably due to water. A signal of 70 (*m*/*z*) corresponding to chlorine also appeared in the catalyst TPD profile above 175 °C, but formation of hydrogen chloride was not observed. Thus, a small part of the Pt

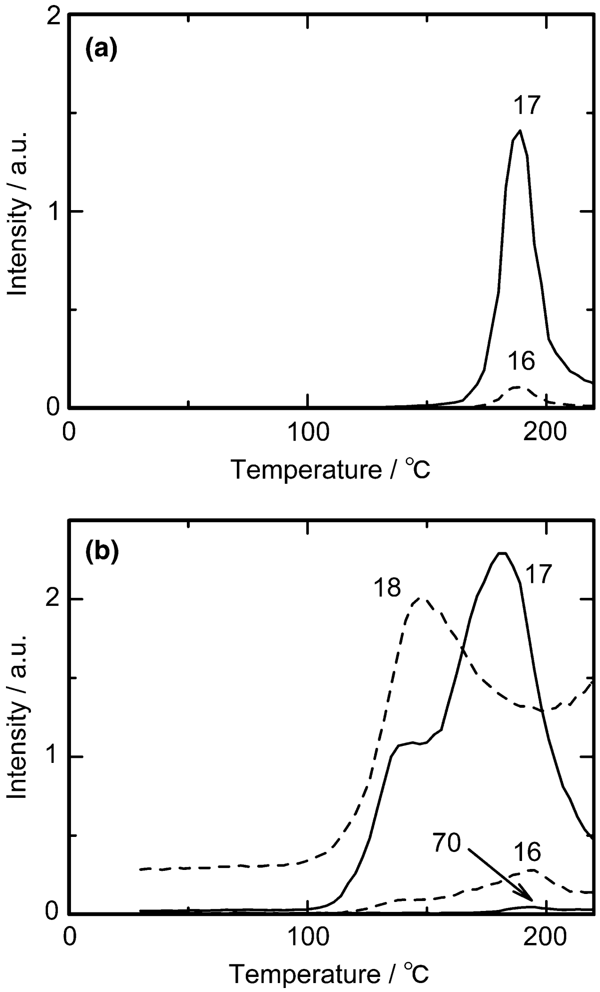

Fig. 6 Temperature programmed desorption of $Pt(NH_3)_4Cl_2$ (**a**) and $Pt(NH_3)_4Cl_2$–PEG/SiO_2 (**b**). Prior to measurement, the samples were evacuated at 100 °C for 2 h, and the temperature was increased at 5 °C min^{-1}

complex in the catalyst releases chorine and this reduces the platinum. However, this reduction did not deactivate the catalyst, because reaction temperature was lower than the reduction temperature.

3.3.3 Extended X-ray Absorption Fine Structure (EXAFS) Analysis of the $Pt(NH_3)_4Cl_2$–PEG/SiO_2 Catalyst

In our previous reports [4], it was concluded from results obtained from EXAFS experiments that the chloride ion of tetraammineplatinum(IV) chloride is coordinated to platinum, which eliminates some of the ammine ligands during the 1-h pretreatment, and that during the reaction, chloride ions originating from trichlorosilane are coordinated to platinum in place of the ammine ligands. The coordination number of the chloride ion increased with time on stream [4]. This is very similar to the change of the yield as a function of time on stream, as shown in Fig. 1b. This strongly suggests that the active species are a platinum complex with a high coordination number of chloride ions [4].

As described above, the active platinum complex in $Pt(NH_3)_4Cl_2$–PEG/SiO_2 was changed during the pretreatment and the reaction. The change of the platinum complex under various treatments was examined using EXAFS. Figure 7 shows Pt L_{III}-edge EXAFS Fourier transforms of tetraammineplatinum(II) chloride dissolved in a PEG supported on silica gel after various treatments. After treatment under a helium stream at 130 °C for 1 h, a shoulder peak at 1.96 Å, which is a value without phase-shift correction because the actual bond length obtained by curve fitting was 2.3 Å was observed along with the main peak at 1.78 Å (the actual bond length obtained by curve fitting was 2.0 Å) assigned to the Pt–N bond, and the shoulder peak intensity increased after treatment for 5 h. This change is probably due to thermal decomposition of tetraammineplatinum(II) chloride into dichlorodiammineplatinum(II); i.e., a part of

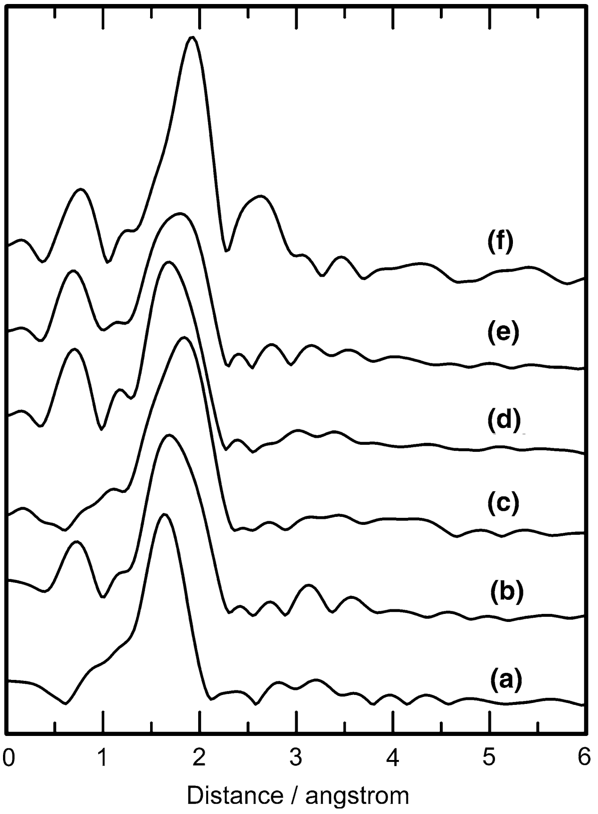

Fig. 7 Pt L_{III}-edge EXAFS Fourier transforms of tetraammineplatinum(II) chloride dissolved in a PEG supported on silica gel (**a**) after He treatment for 1 h (**b**), after He treatment for 5 h (**c**), after He treatment for 1 h and $HSiCl_3$ treatment for 2 h (**d**), after He treatment for 1 h and C_2H_2 treatment for 2 h (**e**), and after He treatment for 1 h, C_2H_2 treatment for 2 h and 4 h reaction (**f**). In all cases, the He treatment temperature was 130 °C. $HSiCl_3$ and C_2H_2 treatments were carried out at 130 °C at 19 kPa of trichlorosilane and 76 kPa of acetylene, respectively

the ammine ligands is eliminated, and chlorine ions are coordinated to form the Pt–Cl bond, which is responsible for the peak at 1.96 Å. After heat treatment for 1 h, trichlorosilane at 19 kPa, or acetylene at 76 kPa, were fed to the reactor for 2 h, and then the catalysts were analyzed by EXAFS. Both peaks at 1.78 and 1.96 Å were observed, and the intensity of the Pt–Cl peak was smaller than that obtained after 5 h treatment in a helium atmosphere. After exposure to acetylene for 2 h, the reaction was carried out for 4 h, and the Pt–Cl peak intensity greatly increased. The coordination numbers of chlorine in Fig. 7b–f, calculated by curve-fitting, were 1.0, 2.0, 0.6, 1.5, and 5.3, respectively. After a long reaction, the coordination number of the chlorine ions reached close to 6; i.e., active species were formed. These results indicate that both trichlorosilane and acetylene are essential for formation of active species.

Hexachloroplatinic acid is the most typical homogeneous catalyst, which is very active [1–3]. As shown in Table 1, K_2PtCl_6–PEG/SiO_2 was also a very active catalyst. These active catalysts have a high coordination number of chlorine ligands. This is consistent with the EXAFS results obtained for $Pt(NH_3)_4Cl_2$–PEG/SiO_2. In the platinum complexes with 6 (or close to 6) chlorine ligands, the ligands may be readily eliminated, and consequently, unsaturated reactants such as acetylene are coordinated to platinum to form an active intermediate for hydrosilylation.

4 Conclusion

Vapor-phase hydrosilylation was carried out using various metal complex catalysts in PEG media supported on silica gel. Tetraammineplatinum(II) chloride and potassium hexachloroplatinate(IV) used as metal complexes showed high activity with high stability. A higher concentration of platinum complex in the PEG led to higher catalytic activity, although a deactivation of the catalyst was later observed. The active species in the catalyst for the reaction of acetylene and trichlorosilane was a platinum complex with a high coordination number of chloride ion ligands, and both trichlorosilane and acetylene were indispensable for active species formation.

Acknowledgment The EXAFS experiments were performed at the Photon Factory with the approval of High Energy Accelerator Research Organization, Japan (Proposal No. 2001G306).

References

1. Voorhoeve RJH (1967) Organohalosilanes: precursors to silicones. Elsevier, Amsterdam
2. Speier JL (1979) Advances in organometallic chemistry, vol 17. In: Stone FGA, West R (eds) Academic Press, New York, pp 213
3. Ojima I (1989) The chemistry of organic silicon compounds, part 2. In: Patai S, Rappoport Z (eds) Wiley, Chichester, pp 1479
4. Okamoto M, Kiya H, Yamashita H, Suzuki E (2002) Chem Commun 1634
5. Rony PR, Roth JF (1975/1976) J Mol Catal 1:13
6. Hjortkjaer J, Scurrell MS, Simonsen P (1979) J Mol Catal 6:405
7. Hjortkjaer J, Scurrell MS, Simonsen P (1981) J Mol Catal 12:179
8. Gerritsen LA, Van Meerkerk A, Vreugdenhil MH, Scholten JJF (1980) J Mol Catal 9:139
9. Gerritsen LA, Herman JM, Klut W, Scholten JJF (1980) J Mol Catal 9:157
10. Gerritsen LA, Herman JM, Scholten JJF (1980) J Mol Catal 9:241
11. Gerritsen LA, Klut W, Vreugdenhil MH, Scholten JJF (1980) J Mol Catal 9:257
12. Gerritsen LA, Klut W, Vreugdenhil MH, Scholten JJF (1980) J Mol Catal 9:265
13. De Munck NA, Notenboom JPA, De Leur JE, Scholten JJF (1981) J Mol Catal 11:233
14. Bond GC (1962) Catalysis by metals. Academic Press, London
15. Grenier-Loustalot MF, Potin-Gautier M, Grenier P (1981) Anal Lett 14:1335
16. Lukevics E, Belyakova ZV, Pomerantseva MG, Voronkov MG (1977) J Organomet Chem Library 5:1
17. Block BP, Roth ES, Simkin J (1960) J Inorg Nucl Chem 16:48