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A novel catalyst containing a platinum complex in polyethylene glycol medium supported on silica gel for vapor-phase hydrosilylation of acetylene with trichlorosilane or trimethoxysilane

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Hydrosilylation of acetylene with trichlorosilane or trimethoxysilane was carried out using a vapor-phase flow reactor with use of tetraammineplatinum(II) chloride in polyethylene glycol medium supported on silica gel as a catalyst, which is an active and thermally stable supported liquid-phase catalyst prepared readily from easily available materials, tetraammineplatinum(II) chloride, polyethylene glycol and silica gel.

Hydrosilylation is one of the most important reactions for formation of carbon–silicon bonds.[1] For example, acetylene hydrosilylation with trichlorosilane and trialkoxysilane gives vinyltrichlorosilane and vinyltrialkoxysilane, respectively, which are useful chemicals as silane-coupling reagents. Generally, hydrosilylation is performed in the liquid phase using a homogeneous catalyst.[1] However, separation of the catalyst from the reaction mixture is troublesome. A vapor-phase flow reaction using a solid catalyst is one of the solutions for this problem. A supported platinum-metal catalyst, such as platinum on activated carbon, is a well-known solid catalyst for hydrosilylation.[1] However, acetylene is strongly adsorbed on the platinum metal surface,[2] probably leading to deactivation of the catalyst in vapor-phase hydrosilylation of acetylene. A non-metal catalyst is suitable for vapor-phase hydrosilylation of acetylene.

A supported liquid-phase catalyst (SLPC) consists of a catalyst component dissolved in a liquid coated on the surface of a porous material, and has both properties of homogeneous and heterogeneous catalysts.[3–5] SLPCs have been used for hydroformylation,[3] selective oxidation[4] and hydrochlorination,[5] and have shown good performances. In these reports, the liquid phase was a molecule with a high boiling temperature or a molten salt.

Here, we report a new type of SLPC and its application to hydrosilylation. A polymer, polyethylene glycol whose vapor pressure is very low at a high temperature,[6] was used as a liquid phase in the SLPC. The catalyst containing tetraammineplatinum(II) chloride in polyethylene glycol medium supported on silica gel showed a high activity for acetylene hydrosilylation as well as a high stability under the reaction conditions.

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) from Fuji Silysia Chemical Ltd., was dried at 170 °C for 24 h in an oven. Tetraammineplatinum(II) chloride ($Pt(NH_3)_4Cl_2{\cdot}H_2O$, 19.4 mg) was dissolved in a mixture of 1.15 g of polyethylene glycol (PEG, average molecular weight: 1000) and 3 mL of water. After adding 2.15 g of the silica gel to the solution, water was further poured into the mixture until the solution had a total volume of 8 mL. The mixture was settled for 24 h and dried using a rotary evaporator to remove water. 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.

Fig. 1 shows time courses of vinyltrichlorosilane yield in the hydrosilylation of acetylene with trichlorosilane over various catalysts. In all runs, a main product was vinyltrichlorosilane, the by-reactions being disproportionation of trichlorosilane and double hydrosilylation of acetylene to form 1,2-bis(trichlorosilyl)ethane. Alumina-supported platinum metal catalyst was active for the hydrosilylation. However, an initial yield of vinyltrichlorosilane was below 40%, and deactivation was serious, probably due to strong adsorption of acetylene on the platinum metal surface. The silica-supported tetraammineplatinum(II) chloride catalyst showed a very high activity up to 2 h of time on stream, and then the yield quickly decreased to 35%. Using the catalyst containing tetraammineplatinum(II) chloride in PEG medium supported on silica gel resulted in a high and stable activity, the yield of vinyltrichlorosilane and the trichlorosilane conversion being 72% and 84%, respectively. When the reaction was continued to 36 h, the activity did not decrease.

Some platinum complexes were tested for the hydrosilylation instead of tetraammineplatinum(II) chloride. Hexachloroplatinic acid, which is the most typical homogeneous catalyst for the hydrosilylation, was used. However, the reaction did not proceed. The EXAFS experiments of the used catalyst revealed that platinum is completely reduced to the metal during the reaction. Potassium hexachloroplatinate also showed a high

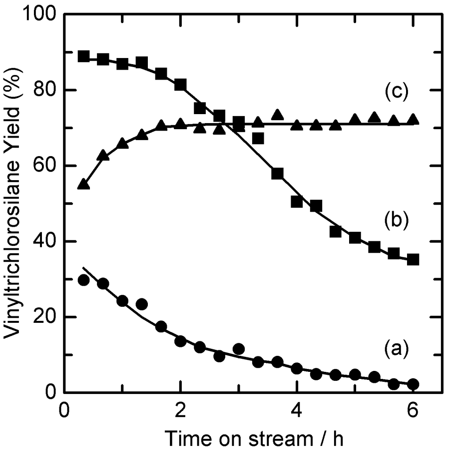

Fig. 1 Time courses of vinyltrichlorosilane yield in hydrosilylation of acetylene with trichlorosilane over platinum metal supported on alumina (a), tetraammineplatinum(II) chloride supported on silica gel (b), and tetraammineplatinum(II) chloride in PEG medium supported on silica gel (c). The reaction was carried out at 150 °C at 19 kPa of trichlorosilane and 76 kPa of acetylene using 300 mg of the catalyst.

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activity, the yield of vinyltrichlorosilane being 67% at 6 h. Platinum(IV) acetylacetonate and potassium tetrachloroplatinate gave only 21% and 30% yield, respectively, at 6 h.

Silica-supported tetraammineplatinum(II) chloride dissolved in PEG catalyst also had a high activity for hydrosilylation with ethylene and propylene. The reaction of trichlorosilane (19 kPa) with ethylene (76 kPa) at 150 °C gave an 86% yield of ethyltrichlorosilane. A by-reaction was only disproportionation of trichlorosilane, tetrachlorosilane yield being 3%. When propylene (76 kPa) was used instead of ethylene, the *n*-propyltrichlorosilane yield was 62%, *iso*-propyltrichlorosilane not being formed.

Using trimethoxysilane (11 kPa) in place of trichlorosilane, hydrosilylation of acetylene (44 kPa) was carried out at 150 °C. Vinyltrimethoxysilane was selectively formed with a high yield, 67%.

Fig. 2 shows Pt L_{III}-edge EXAFS results of the catalyst before and after the reaction. In the EXAFS Fourier transform of tetraammineplatinum(II) chloride (Fig. 2(a)), there was one strong peak at 1.78 Å (without phase-shift correction), which can be assigned to a platinum–nitrogen bond (Pt–N) in square-planar coordination.[7] This Pt–N peak was also observed in the Fourier transform of tetraammineplatinum(II) chloride dissolved in PEG on silica gel (Fig. 2(b)), and its peak intensity did not change, indicating that square-planar coordination still remained. After the pretreatment, a shoulder peak appeared at 1.96 Å, which is attributed to the platinum–chloride bond (Pt–Cl) as mentioned below. Thus, the environment of platinum in the catalyst changed at the pretreatment step. After 1 h of reaction, the Pt–N peak at 1.78 Å disappeared, while the intensity of the Pt–Cl peak at 1.96 Å increased with increasing time on stream till 3 h and then did not change. At 6 h, this Pt–Cl peak intensity was the same as that at 3 h. As mentioned above, the vinyltrichlorosilane yield increased with increasing time on stream till 2 h and then remained at 72%. This change of the yield with time on stream is very similar to that of the intensity change of the Pt–Cl peak at 1.96 Å. This strongly suggests that the platinum species during the reaction is a complex giving the transforms (e) and (f) in Fig. 2. The position of the Pt–Cl peak at 1.96 Å is not the same as those due to Pt–Pt and Pt–O bonds in platinum metal and platinum oxide. Dichlorodiammineplatinum(II), which is well-known as the thermal decomposition product of tetraammineplatinum(II) chloride, gave the Pt–Cl peak at 1.96 Å (two chlorine ligands are coordinated to platinum). The intensity of dichlorodiammineplatinum(II) was, however, lower than those at 1.96 Å in Fig. 2(d–f). The coordination numbers of chlorine resulting from EXAFS analysis were 4.7, 5.6 and 5.3, respectively, and were much higher than 2 in tetraammineplatinum(II) chloride. This suggests that the Pt–Cl peak at 1.96 Å in Fig. 2(d–f) is not due to dichlorodiammineplatinum(II). Thus, it is plausible that the chloride ion is coordinated to platinum with elimination of a part of the ammine ligands from tetraammineplatinum(IV) chloride during the pretreatment, while during the reaction the chloride ion originating from trichlorosilane is coordinated to platinum in place of the ammine ligands. Actually, we have observed that, in the EXAFS transform of potassium hexachloroplatinate in which six chlorines are bonded to platinum with octahedral coordination, the peak due to the platinum–chlorine bond was at the same distance as the Pt–Cl peaks in Fig. 2(e, f), and the intensity and the coordination number of chlorine were also almost the same. Hexachloroplatinic acid, the most typical homogeneous catalyst, is very active for the liquid-phase hydrosilylation, and potassium hexachloroplatinate in polyethylene glycol medium supported on silica was also a very active catalyst for vapor-phase hydrosilylation as mentioned above. These active catalysts have six chlorines and no other ligands. A high coordination number of chlorine present as a sole ligand is consistent with the EXAFS results of tetraammineplatinum(II) chloride dissolved in PEG on silica gel after the reaction.

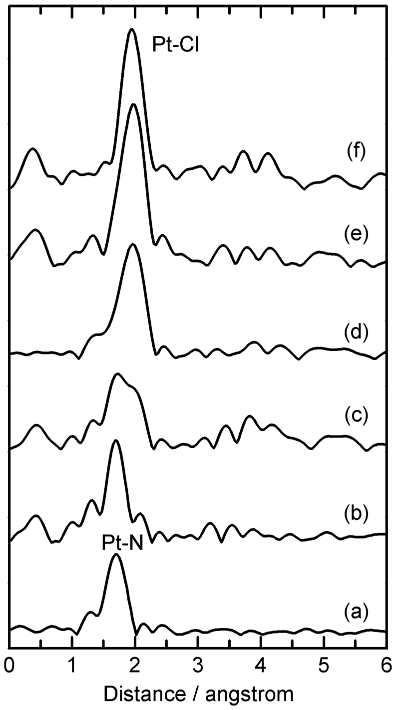

Fig. 2 Pt L_{III}-edge EXAFS Fourier transforms of tetraammineplatinum(II) chloride (a), tetraammineplatinum(II) chloride dissolved in PEG supported on silica gel (b) after the pretreatment (c) and 1 h (d), 3 h (e) and 6 h (f) reaction. The reaction was carried out at 150 °C at 19 kPa of trichlorosilane and 76 kPa of acetylene using 300 mg of the catalyst.

The SLPC reported here can be readily prepared from easily available raw materials, *i.e.* tetraammineplatinum(II) chloride, PEG and silica gel. Furthermore, this catalyst can be handled in an air atmosphere, and its thermal stability is higher than platinum complexes. The SLPC, containing a polymer as a liquid phase, is expected to have applications in various vapor-flow reactions.

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Notes and references

1 R. J. H. Voorhoeve, *Organohalosilanes: Precursors to Silicones*, Elsevier, Amsterdam, 1967; J. L. Speier, *Advances in Organometallic Chemistry, Vol. 17*, ed. F. G. A. Stone and R. West, Academic Press, New York, 1979, pp. 213–279; I. Ojima, *The Chemistry of Organic Silicon Compounds, Part 2*, ed. S. Patai and Z. Rappoport, John Wiley & Sons, Chichester, 1989, pp. 1479–1526.

2 G. C. Bond, *Catalysis by Metals*, Academic Press, London, 1962.

3 P. R. Rony and J. F. Roth, *J. Mol. Catal.*, 1975/76, **1**, 13; J. Hjortkjaer, M. S. Scurrell and P. Simonsen, *J. Mol. Catal.*, 1979, **6**, 405; J. Hjortkjaer, M. S. Scurrell and P. Simonsen, *J. Mol. Catal.*, 1981, **12**, 179; L. A. Gerritsen, A. Van Meerkerk, M. H. Vreugdenhil and J. J. F. Scholten, *J. Mol. Catal.*, 1980, **9**, 139; L. A. Gerritsen, J. M. Herman, W. Klut and J. J. F. Scholten, *J. Mol. Catal.*, 1980, **9**, 157; L. A. Gerritsen, J. M. Herman and J. J. F. Scholten, *J. Mol. Catal.*, 1980, **9**, 241; L. A. Gerritsen, W. Klut, M. H. Vreugdenhil and J. J. F. Scholten, *J. Mol. Catal.*, 1980, **9**, 257; L. A. Gerritsen, W. Klut, M. H. Vreugdenhil and J. J. F. Scholten, *J. Mol. Catal.*, 1980, **9**, 265; N. A. De Munck, J. P. A. Notenboom, J. E. De Leur and J. J. F. Scholten, *J. Mol. Catal.*, 1981, **11**, 233.

4 C. R. Reilly and J. J. Lerou, *Catal. Today*, 1998, **41**, 433, and references therein; H. Komiyama and H. Inoue, *J. Chem. Eng. Jpn.*, 1975, **8**, 310; V. Rao and R. Datta, *J. Catal.*, 1988, **114**, 377.

5 S. A. Panova, G. K. Shestakov and O. N. Temkin, *J. Chem. Soc., Chem. Commun.*, 1994, 977.

6 M. F. Grenier-Loustalot, M. Potin-Gautier and P. Grenier, *Anal. Lett.*, 1981, **14**, 1335.

7 P. Millet, R. Durand, E. Dartyge, G. Tourillon and A. Fontaine, *J. Electrochem. Soc.*, 1993, **140**, 1373.