APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 7, 207–212 (1993)

Catalysis of hydrosilylation, Part XXII: Polymer-protected immobilized platinum complex catalysts for gas-phase hydrosilylation of acetylene*

Bogdan Marciniec,† Zenon Foltynowicz and Mariusz Lewandowski
Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

A platinum catalyst (hexachloroplatinic acid dissolved in ethanol) was immobilized by anchoring via amine and mercapto groups to silica followed by formation of a polymer layer which protected the catalyst against leaching. These catalysts (A and B) as well as precatalysts (S_A-Pt, S_B-Pt) which were not protected by polymer were tested in the gas-phase hydrosilylation reaction of acetylene with trichlorosilane.

The catalytic parameters (yield 80%, selectivity 100%) obtained under optimal conditions prove the advantage of catalyst A over 300 h reaction time by the flow method.

Keywords: Hydrosilylation, acetylene, vinylsilanes, trichlorosilane, platinum catalyst, immobilization, catalysis

INTRODUCTION

Vinyl-substituted silanes constitute a very important class of organosilicon monomers, coupling agents and reagents utilized in organic synthesis. Their industrial production is based mainly on the hydrosilylation of acetylene in the presence of homogeneous and heterogeneous catalysts in liquid and gas-phase systems.[1]

Supported platinum, rhodium and ruthenium complex catalysts have been extensively used in the reaction of trisubstituted chloro- and alkoxysilanes with acetylene in the gas phase, predominantly in a continuous-flow apparatus.[2-8]

The metal complexes have been immobilized via mercapto, phosphine, amine and nitrile ligands anchored on silica. The main failure of these catalysts is, however, reduction to metal colloids and/or leaching during continuous or intensive use in the catalytic process. In order to protect metal colloids coordinated to nitrogen ligands anchored to the support surface against detachment and deactivation, polymerization of *N*-vinyl-substituted ligands onto the surface has been carried out recently.[10, 11]

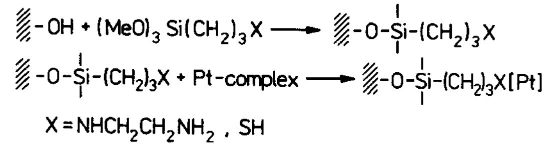
The aim of this work is to report a general method for immobilization of the platinum complex by anchoring via amine and mercapto groups to silica according to Scheme 1.

The immobilization is followed by formation of a polymeric membrane on the surface and the catalyst is subsequently tested in the hydrosilylation of acetylene reaction.

EXPERIMENTAL

Materials

Platinum catalysts were prepared from $H_2PtCl_6 \cdot 6H_2O$ (POCh Gliwice, Poland). The solvents were dried and, as with trichlorosilane, redistilled prior to use. Acetylene (analytical grade), supplied by Polish Technical Gases Co. Ltd, was used as received. Mercaptopropyltriethoxysilane (Union Carbide), {3-[*N*-(2 - aminoethyl)amino]propyl}trimethoxysilane (Fluka AG), hexamethyldisilazane (Aldrich), vinyltrichlorosilane (ABCR), dicyclohexylcarbodiimide (Fluka AG) and methacrylic acid (POCh Gliwice) were commercial products used without further purification.



Scheme 1

---

* For Part XXI see *J. Organomet. Chem.*, 1992, 424: 15.

† Author to whom correspondence should be addressed.

0268-2605/93/030207-06 $08.00

Received 31 July 1992
Accepted 14 November 1992

Table 1 Elemental analysis and specific surface area (*S*) of catalysts and precatalysts

Catalyst	Content (%) C	H	N	Pt	*S* ($m^2 g^{-1}$)
S_A-Pt	7.4	1.8	1.6	7.6	340
S_A-Pt*	13.4	3.1	1.2	6.9	440
S_B-Pt	7.6	2.1	1.7	7.5	330
A	9.5	2.4	1.3	7.2	160
A*	10.2	2.6	1.2	7.0	240
B	9.1	2.2	1.5	7.2	140
Silica	—	—	—	—	360

* After 300 h of reaction on stream

Silica gel MN-Kieselgel-60, from Macharey Nagel Co., Germany, was used as a support.

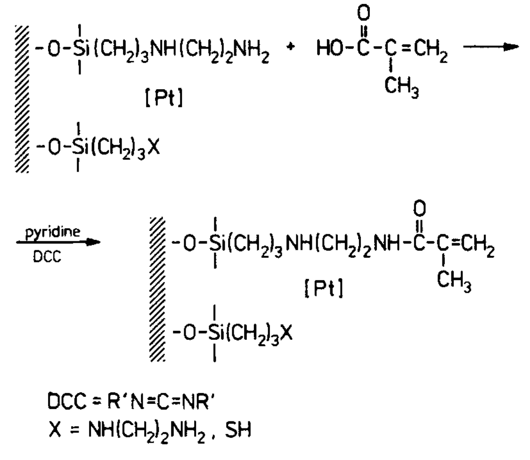
Preparation of supports

Support S_A

Degassed and dried silica gel (5 g) was added to 3.37 g of {3-[*N*-(2-aminoethyl)amino]propyl}trimethoxysilane in 125 cm^3 of benzene. The mixture was refluxed for 16 h with continuous stirring. The silica was then washed with benzene in a Soxhlet apparatus and dried *in vacuo*. After drying, the modified silica was treated with hexamethyldisilazane (benzene solution, 5.3 g in 125 cm^3) for 12 h in order to block the remaining silanol groups (end-capping), then filtered off, extracted, and dried *in vacuo*. The modified silica was white.

Support S_B

Degassed and dried silica gel (5 g; MN-Kieselgel-60) was added to a benzene solution (125 cm^3) of {3-[*N*-(2-aminoethyl)amino]-propyl}trimethoxysilane (1.68 g) and (3-mercaptopropyl)trimethoxysilane (1.50 g) and subsequently treated according to the procedure given for the support S_A. The silica obtained was white.



Scheme 2

Immobilization of platinum complexes

The modified silica supports S_A and S_B (3 g) were each added to 30 cm^3 of an ethanolic solution of H_2PtCl_6, containing 0.01 g Pt cm^{-3}. The mixture was shaken vigorously for 8 h at room temperature, then extracted with ethanol for 6 h in a Soxhlet apparatus, and dried *in vacuo* for 12 h. This resulted in platinum-immobilized precatalysts S_A-Pt and S_B-Pt. All precatalysts were yellow.

Polymeric membrane formation on the surface of catalysts[12]

Precatalyst S_A-Pt or S_B-Pt (3 g) was added to 75 cm^3 of the solvent (benzene/acrylonitrile, 1 : 1) containing 0.26 g of methacrylic acid, 1 cm^3 of pyridine, and 0.62 g of dicyclohexacarbodiimide. The mixture was then refluxed for 8 h. Subsequently, homopolymerized polymethacrylic acid was removed by flotation. The remaining silica was extracted with another portion of the same solvent mixture for 6 h in a Soxhlet apparatus and dried *in vacuo* for 24 h. This led to formation of the membrane-encased platinum catalysts A and B, which were both orange.

Analytical measurements

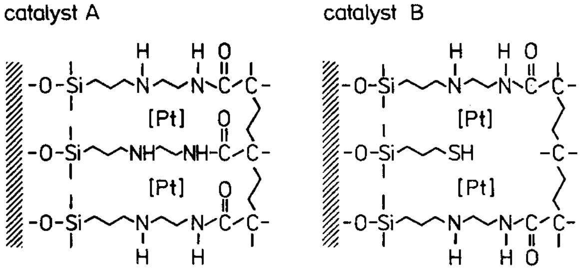
Elemental analyses of the supports and the catalysts (including the metal content of the catalysts) are presented in Table 1.

Electron microscope investigation of supports and catalysts was performed using a transmission electron microscopy (JEOL JEM-7A) and the replica method, with a magnification of ×10 000.

Surface areas of the supports and catalysts were determined from low-temperature nitrogen adsorption measurements performed using a vacuum microbalance (Grawimat–Sartorius Model 4133).

Catalytic activity tests

The procedure and apparatus for catalytic activity measurements have been described previously.[7] The hydrosilylation reaction of acetylene with



Scheme 3

trichlorosilane catalysed by catalysts A and B, and, for comparison, by the S_A-Pt and S_B-Pt precatalysts, was carried out in a flow-type reactor made of Pyrex glass (12 mm diameter, 300 mm long). In a typical experiment, the catalyst (1.8 g) was activated by heating in a stream of acetylene (flow 1 $dm^3 h^{-1}$; 383 K, 1 h). Then a mixture of acetylene and the hydrosilane was sampled at a flow rate of 1.3 $dm^3 h^{-1}$ with a given ratio of acetylene/hydrosilane (10:3). The reaction was followed by GC monitoring at regular time intervals. The effect of reaction conditions, e.g. temperature (100–130 °C), acetylene flow (0.5–1.5 $dm^3 h^{-1}$) and the amount of catalyst (0.6–3.0 g) on the reaction yield was examined before the main catalytic tests.

The reactor was operated differentially and therefore the initial rate of hydrosilylation can be expressed as Eqn [1].[7,13]

$$r = \frac{Y}{100W/f} \qquad [1]$$

where Y is the yield of vinylsilane (%), $W(g)$ is the weight of catalyst used, f (μmol s^{-1}) is the flow rate of hydrosilane and r is expressed in μmol of vinylsilane (at 0.1 MPa and 20 °C) per g of metal and per second.

RESULTS AND DISCUSSION

Platinum precatalysts were prepared using well-known methods. The commercially available {3-[N-(2-aminoethyl)amino]propyl}trimethoxysilane dissolved in benzene was bound to the silica surface via siloxane bonds in support S_A. Similarly, 3-mercaptotrimethoxysilane was linked to the silica together with the aminosilane in

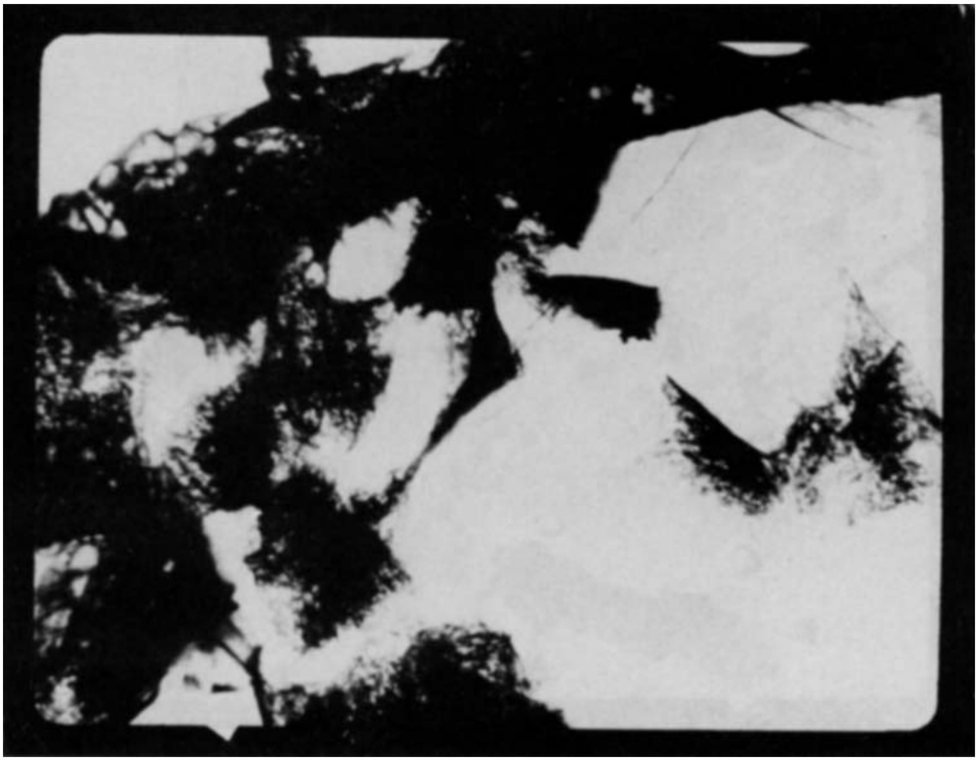


Figure 1 Transmission electron microscopy (×10 000, replica method) of the surfce of catalyst A.

support S_B. Formation of the supports is described by the first equation in Scheme 1. After immobilization of the platinum complex onto these supports, the precatalysts S_A-Pt and S_B-Pt were obtained according to the second equation in Scheme 1. Next S_A-Pt and S_B-Pt were subjected to a procedure for fixation of polymer layers, involving reaction of amino-functional silicas with methacrylic acid and resulting in formation of amide bonds[14] according to Scheme 2.

This reaction was followed by methacrylic polymerization onto the surface, finally forming the protective polymer layer. An increase in carbon and hydrogen content in A and B as compared with S_A and S_B is evidence for such a process (Table 1).

The idealized schemes for the possible structure of the catalysts A and B are given in Scheme 3. However, copolymerization of methacrylate attached to the silica with methacrylic acid monomer also leads to formation of a final polymeric layer. It could clearly be shown that both catalysts A and B are apparently mesoporous.

Immobilization of chloroplatinic acid under the conditions described in the Experimental section presumably leads to the platinum complex being linked to silica via amino (mercapto) ligands. The microscope photographs show that finely dispersed platinum is present on the silica prior to the reaction (Fig. 1).

During the continuous hydrosilylation process, platinum is reduced by silicon hydride ($SiHCl_3$) to give aggregates, (1200–1700 Å) but these are still linked to the surface (Fig. 2).

Recent experiments described by Lewis and coworkers suggested that colloidal platinum was a key intermediate in platinum complex precursors (e.g. Speier and Karstedt catalysts) for 'homogeneously' catalysed hydrosilylation in a liquid phase.[15–17] Colour changes in the solution are directly related to the changes that occur in the colloid structure and its catalytic activity.[17] With the immobilized catalysts, however, visible colour changes are presumably due to aggregates linked to the surface rather than to real metal colloids.

Polymeric coating, in addition, preserves the platinum catalyst against leaching. No marked change in platinum content after many hours of catalysis has been observed (Table 1). During this process, however, high-boiling by-products are

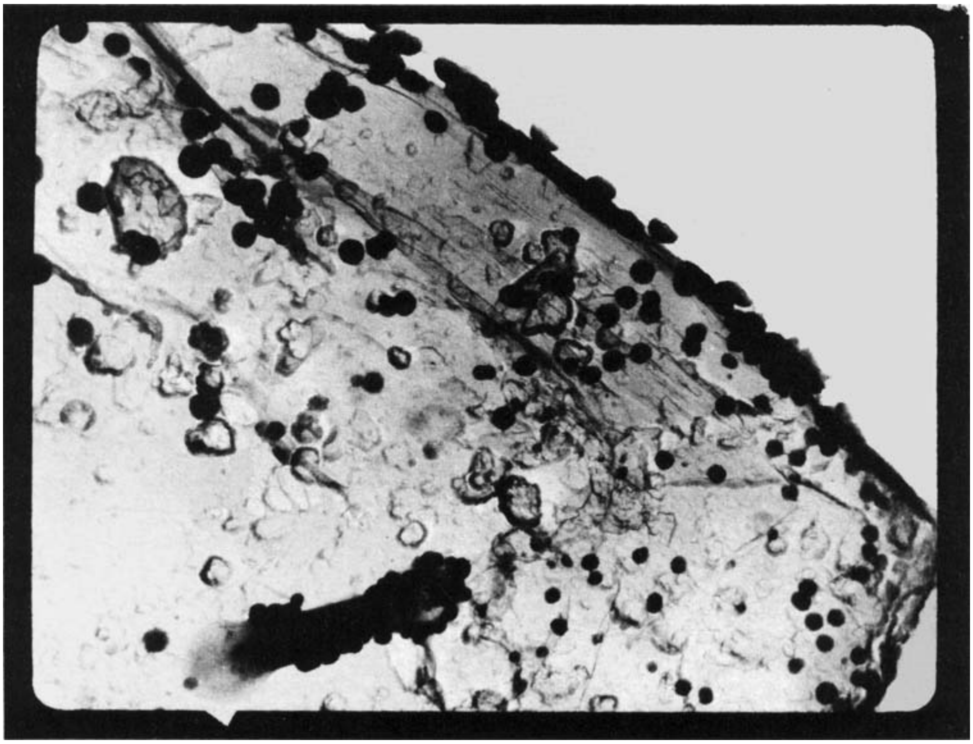


Figure 2 Transition electron microscopy (×10 000, replica method) of the surface of the catalyst A after long-term catalytic process.

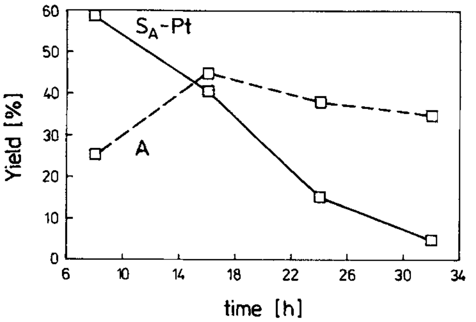


Figure 3 Yield of vinyltrichlorosilane from the hydrosilylation of acetylene by trichlorosilane in the presence of precatalyst S_A-Pt (—) and catalyst A (---). $T = 100\,°C$; $f_{C_2H_2} = 32.9\ \mathrm{mmol\ h^{-1}}$; $f_{SiH} = 20\ \mathrm{mmol\ h^{-1}}$.

deposited on the surface of S_A-Pt and S_B-Pt precatalysts and therefore a distinct increase in the carbon and hydrogen content after long-term reaction is observed. In contrast, much lower deposition of by-products is noted for polymer-protected catalysts (Table 1).

Whilst modification of silica with aminosilanes little changes the specific surface area, formation of a polymeric membrane decreases it considerably due to pore blocking by the polymeric layer. However, during many hours' use of the catalyst, the membrane undergoes transformations, becoming more porous (see Figs 1 and 2). A marked enhancement of surface area (from 160 to 240 $m^2\ g^{-1}$) is observed as a result of this process.

In this work we have tried to test the platinum complex as an immobilized catalyst on silica surfaces in gas-phase and in heterogeneous hydrosilylation.

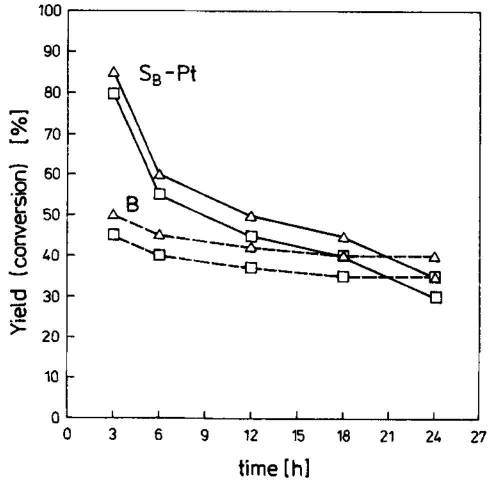


Figure 4 Conversion of trichlorosilane (△) and yield of vinyltrichlorosilane (□) from the hydrosilylation of acetylene in the presence of precatalyst S_B-Pt (—) and catalyst B (---). $T = 100\,°C$; $f_{C_2H_2} = 32.9\ \mathrm{mmol\ h^{-1}}$; $f_{SiH} = 20\ \mathrm{mmol\ h^{-1}}$.

Table 2 Effect of temperature on the yield (Y) of vinyltrichlorosilane and catalytic activity (r) of the catalyst A in the hydrosilylation of acetylene by trichlorisilane

Temperature (°C)	Y (%)	r [μmol $g^{-1}\ s^{-1}$]
100	60	2.8
110	68	3.2
120	65	3.0
130	35	1.6

Flow rates $f_{C_2H_2} = 44.6\ \mathrm{mmol\ h^{-1}}$; $f_{Si\text{-}H} = 20\ \mathrm{mmol\ h^{-1}}$; mass of catalyst A, $c_k = 1.2$ g; reaction time = 16 h.

The polymer-protected platinum catalysts (A and B) prepared, as well as the precatalysts S_A-Pt and S_B-Pt for comparison, were used in the hydrosilylation of acetylene by trichlorosilane by the reaction:

$$HSiCl_3 + HC{\equiv}CH \rightarrow CH_2{=}CHSiCl_3 \quad [2]$$

Vinyltrichlorosilane was detected by GLC and identified as the only main product, accompanied by traces of $SiCl_4$ which had been present in the $HSiCl_3$.

In contrast to reactions in gas-phase systems catalysed by ruthenium and rhodium complexes[7, 8] as well as to most liquid-phase catalytic reactions (e.g. Ref. 9), no double-hydrosilylated product [i.e. bis(trichlorosilyl)ethane] or no redistribution of $HSiCl_3$ was detected under the conditions used in this work.

Selected data for the main series of reactions involving hydrosilylation by trichlorisilane are presented in Figs 3 and 4. Under mild non-optimal conditions for the reaction, a drastic decrease in the catalytic activity of precatalysts S_A-Pt and S_B-Pt was observed. Protection of the immobilized catalysts by polymer lowers the

Table 3 Effect of flow rate of acetylene ($f_{C_2H_2}$) on the yield (Y) of vinyltrichlorosilane and catalytic activity (r) of the catalyst A in the hydrosilylation of acetylene by trichlorisilane

$f_{C_2H_2}$ (mmol h^{-1})	Y (%)	r (µmol $g^{-1}\ s^{-1}$)
22.3	35	1.6
32.9	60	2.8
44.6	68	3.15
55.8	70	3.3
67.0	71	3.4

Flow rate $f_{SiH} = 20\ \mathrm{mmol\ h^{-1}}$; mass of catalyst A, $c_k = 1.2$ g; $T = 110\,°C$; reaction time = 16 h.

Table 4 Effect of the mass of the catalyst A (c_k) on the yield (Y) and catalytic activity (r) in the hydrosilylation of acetylene by trichlorosilane

c_k (g)	Y (%)	r (μmol g^{-1} s^{-1})
0.6	35	3.3
1.2	68	3.15
1.8	79	2.5
2.4	82	1.9
3.0	84	1.6

Flow rates $f_{C_2H_2} = 44.6$ mmol h^{-1}, $f_{Si\text{-}H} = 20$ mmol h^{-1}; $T =$ 110 °C; reaction time = 16 h.

initial yield as well as the conversion of the silane; however, it helps to maintain the catalytic activity at a stable level for a long time. Catalyst A even shows a marked growth in the yield for the first 16 hours.

Grafting copolymerization of methacrylate onto the surface resulting in formation of a membrane structure and a drastic diminution of the surface area (numbers of micropores) made the reagent diffusion more difficult. This seems to be the reason why a prolonged activation period for the catalyst and an increase in the catalytic activity have been observed. In order to optimize the hydrosilylation process, the effects of temperature, the acetylene flow rate, the ratio acetylene to silane and the amounts of catalyst were examined using catalyst A. The respective data, presented in Tables 2–4, allow us to establish the following optimum conditions for a long-term reaction: 110 °C, $f_{C_2H_2} = 1$ dm^3 h^{-1} (37.2 mmol h^{-1}), $f_{HSi} = 2$ cm^3 h^{-1} (9.3 mmol h^{-1}) and 1.8 g catalyst. Any higher amounts of the catalyst, although it would slightly increase the conversion of the reactants, would cause a significant increase in resistance of the catalyst bed, on occasion making gas flow impossible. Figure 5 illustrates the high and stable activity and selectivity of catalyst A observed over 300 h flow of reagents, i.e. almost 80% yield. Such yield and selectivity (100%) makes this catalyst very effective for production of vinyltrichlorosilane.[18]

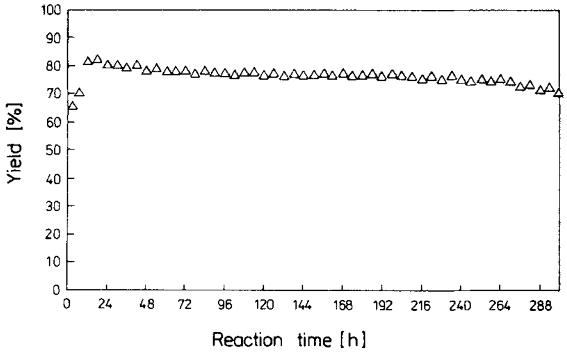


Figure 5 Yield of vinyltrichlorosilane from the hydrosilylation of acetylene in the presence of catalyst A. $T = 110$°C; $f_{C_2H_2} = 44.6$ mmol h^{-1}; $f_{SiH} = 20$ mmol h^{-1}; mass catalyst A, $c_k = 1.8$ g.

CONCLUSIONS

Immobilization of a platinum complex by anchoring via amine to silica, followed by protection of the catalyst against leaching via formation of a polymeric membrane, makes the catalytic system very active, selective and stable during a long-term hydrosilylation of acetylene by trichlorosilane in a gas-phase flow method. Under optimum conditions, the selected catalyst A gives almost 80% yield of vinyltrichlorosilane and 100% selectivity during 300 h of continuous reaction on-stream.

REFERENCES

1. Marciniec, B (ed) *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford, 1992, Chapter 2
2. Kraus, M *Coll. Czech. Chem. Commun.*, 1974, 39: 1318
3. Majstrikova, M, Rericha, R and Kraus, M *Coll. Czech. Chem. Commun.*, 1974, 39: 135
4. British Patent 670 617 (1949)
5. US Patent 2 632 013 (1953)
6. Fr. Pat. 1 390 999 (1965)
7. Marciniec, B, Foltynowicz, Z, Urbaniak, W and Perkowski, J *Appl. Organomet. Chem.*, 1987, 1: 267
8. Marciniec, B, Foltynowicz Z and Urbaniak, W *Appl. Organomet. Chem.*, 1987, 1: 459
9. Hu, C Y, Hau, X M and Jiang, Y Y *J. Mol. Catal.*, 1986, 35: 329
10. Hirai, H, Ohataki, M and Komiyama M *Chem. Lett.*, 1986, 269; 1987, 149
11. Wang, Y, Liu, H and Jiang, Y *J. Chem. Soc., Chem. Commun.*, 1989, 1878
12. Polish Patent P-295 178 (1992)
13. De Munch, N A, Verbrugge, M W and Scholten, J J F *J. Mol. Catal.*, 1981, 10: 313
14. Haller, I *J. Am. Chem. Soc.*, 1978, 100: 8050
15. Lewis, L N and Lewis, N *J. Am. Chem. Soc.*, 1986, 108: 7228
16. Lewis, L N *J. Am. Chem. Soc.*, 1990, 112: 5998
17. Lewis, L N, Uriarte, R J and Lewis, N *J. Catal.*, 1991, 127: 67
18. Polish Patent P-295 177 (1992)