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Catalysis of hydrosilylation. XV. A poly(phosphino-organosiloxanyl)silicate-supported rhodium(I) catalyst for gas-phase hydrosilylation of acetylene*

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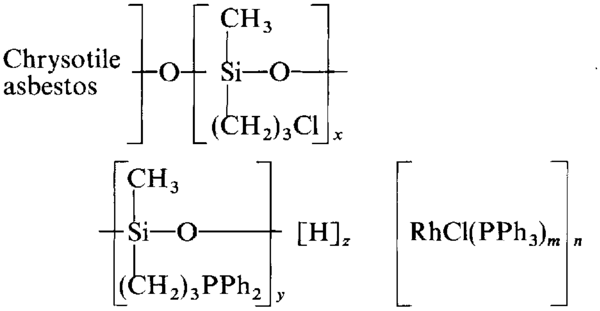
Wilkinson's complex [RhCl(PPh$_3$)$_3$], anchored to phosphino-organosiloxane macromolecules grafted onto chrysotile asbestos, appeared to be an unusually effective and selective catalyst for the synthesis of vinylsilanes via gas-phase hydrosilylation of acetylene, particularly by methyldichlorosilane in a continuous-flow microreactor as well as in a laboratory reactor. Catalytic and kinetic parameters show an advantage for the catalyst based on the chrysotile–polyorganosiloxane support (catalyst CHR–Rh) over the phosphinated silica (catalyst A).

Keywords: Hydrosilylation, acetylene, vinylsilanes, Wilkinson's catalyst, chrysotile asbestos, catalysis, methyldichlorosilane, trichlorosilane

INTRODUCTION

Silica-supported rhodium and ruthenium complexes have proved to be effective catalysts for the hydrosilylation of acetylene by trichlorosilane carried out in a microreactor in the gas phase.[1] Such a flow method can be employed for the industrial synthesis of vinyltrichlorosilane, which is commercially used as an important coupling agent and reagent in organic synthesis.

The aim of this work is to extend this catalytic method for the synthesis of methylvinyldichlorosilane—one of the fundamental organosilicon monomers—as well as to optimize the catalysts and supports used. In addition, our previous examinations have shown a high catalytic activity for rhodium(I) complexes anchored to phosphino-organosiloxane grafted onto chrysotile (structure I) in the hydrosilylation of the C=C bond of olefins[2] occurring in the liquid phase.



$$\text{Chrysotile asbestos}\!-\!O\!-\!\left[\overset{CH_3}{\underset{(CH_2)_3Cl}{Si}}\!-\!O\right]_x\left[\overset{CH_3}{\underset{(CH_2)_3PPh_2}{Si}}\!-\!O\right]_y[H]_z\ \left[RhCl(PPh_3)_m\right]_n$$

I; $m = 0$–2; $z = 0, 1$; $x:y = 3:1$

Our preliminary data confirm the possibility of successfully employing a phosphinated-silica-supported Rh(I) complex also in the gas-phase hydrosilylation of acetylene[1] in contrast to reported methods of vinylsilane synthesis which proceed in the liquid phase.[3–8] The latter involved various homogeneous[3–5] and heterogeneous[6–8] complexes mainly of rhodium, ruthenium and platinum in the addition of silicon hydrides to acetylene. However, they do not seem to be feasible for the industrial production of vinylsilanes, particularly methylvinyldichlorosilane and vinyltrichlorosilane. Therefore, our experiments, carried out predominantly in a flow microreactor, are also aimed at validating the catalysts for the industrial synthesis of vinylsilanes using a laboratory reactor.

EXPERIMENTAL

Trichlorosilane and methyldichlorosilane were commercially available and distilled prior to use.

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*For Part XIV see *J. Mol. Catal.*, 1987, 42: 195.

Vinylmethyldichlorosilane, methyltrichlorosilane, ethyltrichlorosilane and ethylmethyldichlorosilane (Flucka) were used as received. Wilkinson's complex [$RhCl(PPh_3)_3$] was prepared according to known procedures. Catalyst A was obtained by equilibration of Wilkinson's complex with phosphinated silica. For catalyst CHR–Rh, $RhCl(PPh_3)_3$ was anchored to phosphino-organosiloxane grafted onto the chrysotile.

Materials and details of procedures for preparation of supports and catalysts as well as results of their elemental analysis have been described elsewhere.[1,2]

Procedure

The procedure and apparatus for catalytic examinations as well as the method for data treatment were also previously reported.[1] The reactions of acetylene with methyldichlorosilane (or trichlorosilane) catalysed by a poly(phosphino-organosiloxanylo)silicate-supported rhodium(I) catalyst (CHR–Rh) and by a phosphinated silica-supported Rh(I) catalyst (A) were carried out in a flow-type microreactor. In a typical experiment the catalyst (0.3–0.6 g) was degassed in a stream of purified nitrogen (393 K, 1 h) and activated by heating in a stream of acetylene (393 K, 1.5 h). Then a mixture of acetylene and hydrosilane was sampled at a flow rate of usually 1.0 $dm^3 h^{-1}$, with a molar ratio of acetylene:hydrosilane from 5:1 to 10:1 (excess of acetylene). The process was carried out in the temperature range 353–423 K. The hydrosilylation reactions were monitored periodically by GC analysis of the liquid or gaseous phase.[1] The products obtained were identified by comparison of their retention times with those of authentic samples. Repeatable data of the hydrosilane conversion and other catalytic hydrosilylation process parameters were obtained after a reaction course of 1 h at a given temperature.

Stability tests were performed in a laboratory-scale reactor (Pyrex glass, 10 cm^3 capacity) operating with continuous flow conditions. Typical reaction conditions were: amount of catalyst, 8 g; reaction mixture flow, 2.5 $dm^3 h^{-1}$; temperature, 413 K. The procedures for catalyst standardization, as well as other conditions, were the same as in the reactions with the micro-reactor. The reaction mixture was collected over the whole test period and analysed by GC after its completion. In addition, the reaction was followed by GC monitoring at regular time intervals.

RESULTS AND DISCUSSION

The prepared chrysotile-supported complex of rhodium(I) (catalyst CHR–Rh) was used in the gas-phase hydrosilylation of acetylene by methyldichlorosilane and trichlorosilane. Selected catalytic data for these reactions are presented in Tables 1 and 2, respectively.

The results include the conversion of hydrosilane (C_H) (the reactions were carried out with excess of acetylene), the yield of vinylsilane, Y, as well as the selectivity of the reaction products, S_n. Also in the tables the respective results for the silica-supported Rh(I) complex (catalyst A) are presented and compared with the data from previous work.[1]

As is known (see the Scheme in Ref. 1), hydrosilylation of acetylene by silicon hydrides leads to the main product (**1**) according to Eqn. [1]; it is accompanied by the products of double hydrosilylation ($(Cl_2CH_3SiCH_2)$) (**2**) or $(Cl_3SiCH_2)_2$, of hydrosilane redistribution CH_3SiCl_3 (**3**) or $SiCl_4$

Table 1 Effect of catalyst type on the conversion (C_H) of the hydrosilane, the yield (Y) of vinylmethyldichlorosilane and the selectivity (S) of the products (GC) for the reaction of methyldichlorosilane with acetylene at 140°C

Catalyst	Weight (g)	F (mmol h^{-1})[c]		C_H (%)	S_n (%)				Y (%)
		HC≡CH	$HSiCl_2CH_3$		1	2	3	4	
CHR–Rh	0.32	19.8	2.2	95	83	—	12	2	79
CHR–Rh	0.32	22.8	2.6	90	82	—	10	4	74
A	0.58	22.8	2.6	63	70	—	20	5	44
CHR–Rh[a]	8.0	110.0	11.2	93	80	4	12	4	74
CHR–Rh[a,b]	8.0	110.0	11.2	85	80	2	10	3	68

[a] Laboratory reactor, [b] Catalyst 45 h on stream, [c] F, flow rate.

Table 2 Effect of flow rate (F) of acetylene and trichlorosilane on hydrosilane conversion (C_H), yield (Y) of vinyltrichlorosilane and selectivity (S) of the products (GC) for the reaction of trichlorosilane with acetylene catalysed by the chrysotile-supported rhodium catalyst (CHR–Rh) at 140°C

Catalyst	Weight (g)	F (mmol h^{-1}) HC≡CH	F (mmol h^{-1}) $HSiCl_3$	C_H (%)	S_n (%) 1	S_n (%) 2	S_n (%) 3	S_n (%) 4	Y (%)
CHR–Rh	0.32	22.8	2.6	82	78	—	13	5	64
A[a]	0.58	22.8	2.6	100	70	—	19	10	70
CHR–Rh	0.32	45.0	6.4	42	90	3	5	—	38
CHR-Rh	0.32	110.0	6.0	75	75	3	15	4	56
CHR-Rh[b]	8.0	110.0	22.0	93	71	2	20	8	66
CHR-Rh[b,c]	8.0	110.0	22.0	75	80	5	10	3	60

[a]See Ref. 1, [b]Laboratory reactor, [c]Catalyst 72 h on stream.

as well as products of hydrogenating hydrosilylation of acetylene, i.e. ethyl-substituted silanes, $C_2H_5SiCH_3Cl_2$ (**4**) or $C_2H_5SiCl_3$.

$$\equiv Si\text{-}H + CH\equiv CH \rightarrow \underset{(\mathbf{1})}{CH_2{=}CHSi\equiv} \qquad [1]$$

Traces of other unidentified monomeric by-products were also recorded under some conditions. The very reactive second product of the redistribution (H_2SiCl_2 or H_2SiCH_3Cl) forms mainly polymeric adducts with acetylene which cannot be identified by GC.[1] A gas-chromatogram illustrating the products of the addition of methyldichlorosilane to acetylene is given in Fig. 1. Chromatograms showing the products of the reaction occurring with trichlorosilane as well as the redistribution of hydrosilane were given previously.[1]

The results given in Table 1 show a substantial effect of the polysiloxane chain grafted onto the chrysotile support structure on the catalytic behaviour of the immobilized Wilkinson complex. This heterogeneous catalyst (CHR–Rh) is an unusually effective and selective catalyst for the synthesis of vinylmethyldichlorosilane. High conversion of the hydrosilane as well as high yield and selectivity for vinylmethyldichlorosilane enable us to apply this method on the larger scale in a laboratory reactor. A five-fold increase in both substrate flows has a very slight influence on the yield and selectivity of the products. The results indicate the possibility of the technological application of the system examined for the synthesis of vinylmethyldichlorosilane.

In contrast to the reaction with methyldichlorosilane, the addition of the trichlorosilane to acetylene occurs with a very similar yield regard-

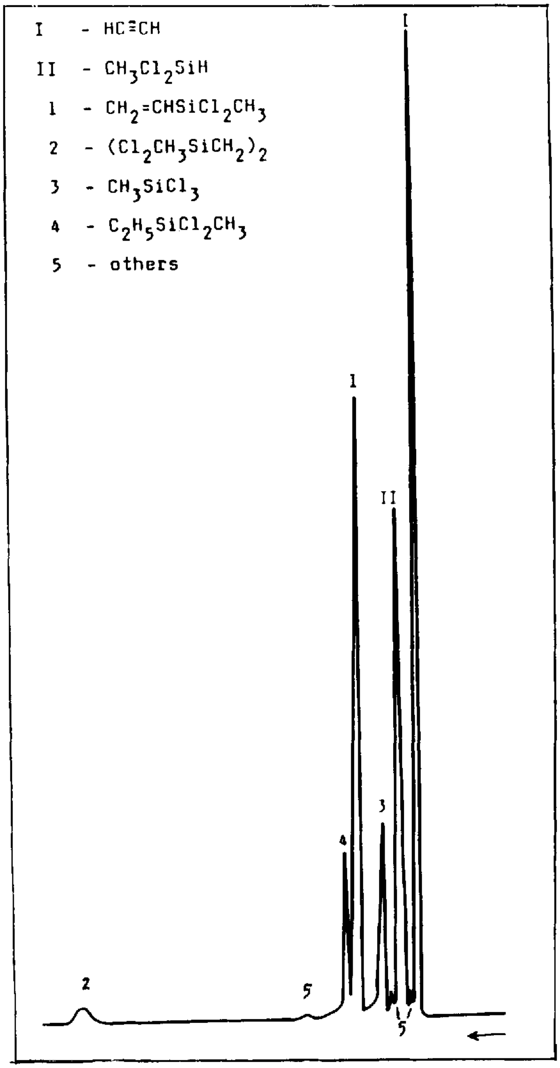

Figure 1 An example of GC separation of the reaction mixture.

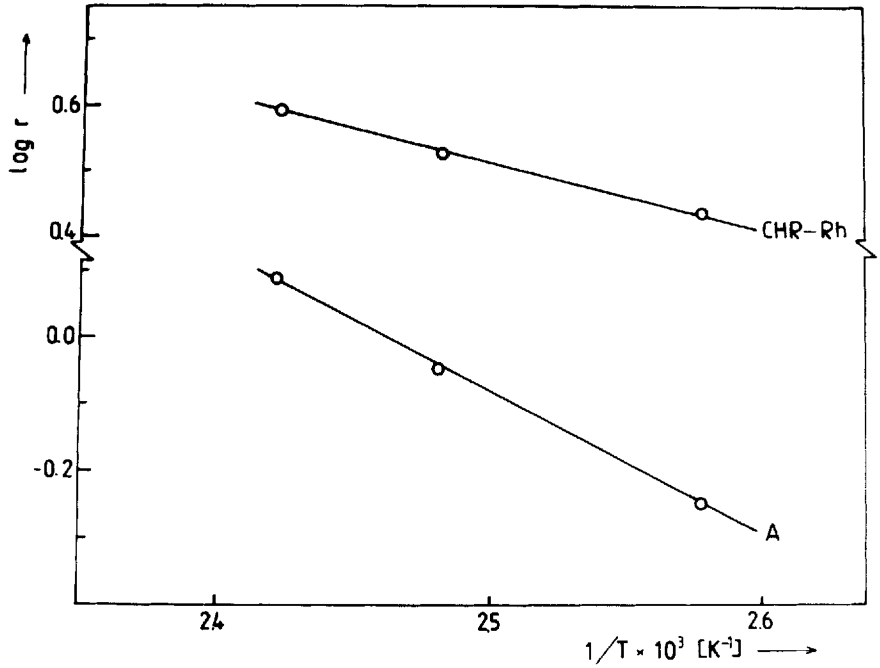

Figure 2 Arrhenius plot for gas-phase hydrosilylation of acetylene by methyldichlorosilane.

less of the support for the immobilization of Wilkinson's catalyst (Table 2) although amounts of by-products and conversion of the hydrosilane are apparently lower in the case of the chrysotile–polysiloxane support. Nevertheless, these experiments carried out in the laboratory reactor also suggest the possibility of increasing scale for vinylsilane production.

The kinetic and activation parameters, compiled in Table 3, illustrate the advantage of the chrysotile–polyorganosiloxane-supported rhodium catalyst over the silica-supported one for the reaction of methyldichlorosilane with acetylene.

Table 3 Catalytic activity (r) of the catalysts A and CHR–Rh, and activation energy E_a for the hydrosilylation of acetylene by methyldichlorosilane

	r ($\mathrm{cm^3\,g^{-1}\,s^{-1}}$)		
Catalyst	115°C	140°C	E_a ($\mathrm{kJ\,mol^{-1}}$)
A	0.57	1.30	29.3 ± 3.3
CHR–Rh	2.92	4.16	19.2 ± 2.1

$\Delta r \cong 0.03$.

The initial rate of the reaction, r, for the chrysotile supported catalyst is 3–5 times that for the silica-supported one. The activation energy determined from an Arrhenius plot (Fig. 2) is markedly lower for the former. The most characteristic features of the two supports are parameters determining the amounts of the bonding phosphine ligand and the coordinating rhodium complex in the surface unit (i.e. phosphorus and rhodium per surface unit respectively in $\mathrm{mmol\,m^{-2}}$) which are equal to 0.66 and 0.29 for the chrysotile support and 0.17 and 0.04 for the silica one. They can additionally explain the unusual properties of the polyorganosiloxane–silicate support under study.

We can conclude that the Wilkinson's complex immobilized on a chrysotile–polyorganosiloxane support, including 3-diphenylphosphinopropylsiloxanyl- and 3-chloropropylsiloxanyl- units in the polymeric chain, is very effective in the hydrosilylation of acetylene by trichlorosilane and methyldichlorosilane occurring in the gas phase. This may become a very useful method, particularly for the production of vinylmethyldichlorosilane, on an industrial scale.

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