

## HYDROSILYLATION CATALYSED BY RHODIUM COMPLEXES ON POLYMERS WITH DIFFERENT DEGREE OF CROSS-LINKING\*

I. DIETZMANN\*\*, D. TOMANOVÁ and J. HETFLJŠ

*Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbátov*

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A series of polymer-supported rhodium catalysts was prepared by reaction of tetracarbonyldichlorodirrhodium with dimethylaminomethylated styrene-divinylbenzene copolymers of different degree of cross-linking (10, 15, 25, 40, 50, 60%). Texture changes during the preparation of the catalysts were followed by surface area measurements and by porosimetry. The dispersity of the metal on the surface of the catalysts was determined by titration of the reduced catalyst with oxygen. The activity and selectivity of the catalysts was tested by several hydrosilylation reactions. The activity of the catalysts increased with their increasing surface area and pore radius. All the catalysts showed similar selectivity which was comparable with the selectivity of the soluble rhodium complex, tetracarbonyldichlorodirrhodium. Possible reasons of these phenomena are briefly discussed.

Catalysts with metallic component coordinately bound to a polymeric skeleton bearing a suitable ligand constitute a new class of heterogeneous catalysts<sup>1-5</sup> which are active in a variety of organic reactions<sup>1</sup> and are acting similarly as complex homogeneous catalysts. In a previous work<sup>6</sup> we briefly reported on the use of polymer-supported rhodium complexes as hydrosilylation catalysts. As a continuation of this study in the present work we were concerned with the effect of varying degree of cross-linking of a polymeric component on the activity, physical properties and texture of these catalysts. For this purpose we used a styrene-divinylbenzene copolymer bearing dimethylamino groups as a macromolecular ligand. The different cross-linking of the copolymer was achieved by varying the styrene to divinylbenzene ratio. The catalysts were prepared by reaction of the polymeric ligand with tetracarbonyldichlorodirrhodium. As found by Rollmann<sup>7</sup>, this bridge-splitting reaction leads to the rhodium complexes of well-defined structure.

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\*\* On leave from the Bereich Komplexkatalyse, Zentral-Institut für organische Chemie, AW der DDR Rostock, DDR.

TABLE I  
Texture and Activity of Rhodium Catalysts

Sample	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	P <sub>4</sub>	P <sub>5</sub>	P <sub>6</sub>
Basic copolymer						
Divinylbenzene, %	10	15	25	40	50	60
Surface area, m <sup>2</sup> /g	25	83	124	212	226	247
Chloromethylated copolymer						
Chlorine, %	12.15	8.52	5.28	5.36	6.46	3.96
Surface area, m <sup>2</sup> /g	31	72	89	111	146	271
Dimethylaminomethylated copolymer						
Nitrogen, %	3.64	2.37	1.37	0.80	0.96	0.90
Surface area, m <sup>2</sup> /g	39	84	110	193	252	325
Catalyst						
Rhodium, %	2.17	2.20	2.08	3.87	2.15	2.25
Surface area, m <sup>2</sup> /g by nitrogen	58	90	118	201	282	287
by n-hexane	36	104	134	171	188	229
by benzene	60	137	169	195	228	258
True density, g/cm <sup>3</sup>	1.110	1.140	1.165	1.215	1.160	1.240
Apparent density, g/cm <sup>3</sup>	0.845	0.560	0.492	0.385	0.345	0.378
Pore volume, ml/g						
total	0.289	0.912	1.175	1.774	2.030	1.839
0–4000 Å from n-hexane adsorption	0.257	1.047	0.996	1.105	1.091	1.402
75–75 000 Å by mercury porosimetry	0.228	0.830	1.075	1.661	1.811	1.665
Most frequent pore radius, Å,						
from n-hexane adsorption	14	20	20	20	20	20
Pore size distribution (%)		300	190	80	90	
from mercury porosimetry						
75–300 Å	98	90	61	51	46	35
300–1 000 Å	2	6	29	28	37	42
>1 000 Å	0	4	10	21	17	23
Reduced catalyst						
Titration with oxygen, ml/g	0.480	0.676	0.455	1.442	2.579	2.771
Ratio O/Rh	0.20	0.28	0.20	0.34	1.10	1.13
Surface area of metallic rhodium, m <sup>2</sup> /g	49	64	49	84	270	277

TABLE I  
(Continued)

Sample	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	P <sub>4</sub>	P <sub>5</sub>	P <sub>6</sub>	
Activity tests							
<i>Reaction</i>	<i>Products</i>		<i>Yields in per cent</i>				
1-Heptene + HSiCl <sub>3</sub>	1-heptyltrichlorosilane	0	0	3	14.3	28.3	72.0
Styrene + HSiCl <sub>3</sub>	1-trichlorosilyl-1-phenylethane and -2-phenylethane	0	0	0.5	2.5	4.5	42.0
Selectivity tests							
Styrene + HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> : A/B ratio <sup>a</sup>	1.6	1.2	1.4	1.6	1.5	1.1	
1,3-Butadiene + HSi(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> : the <i>trans</i> - to <i>cis</i> -2-butenyltriethoxysilane ratio	—	6.7	6.5	6.2	6.3	6.6	
3,3-Dimethyl-1-butene + 1-heptene + HSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> : <i>k</i> <sub>rel</sub> <sup>b,c</sup>	0.92	0.78	— <sup>d</sup>	0.90	0.85	0.84	
4,4-Dimethyl-1-pentene + 1-heptene + HSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> : <i>k</i> <sub>rel</sub> <sup>b</sup>	— <sup>d</sup>	0.20	— <sup>d</sup>	0.20	0.21	0.20	

<sup>a</sup> A 1-triethoxysilyl-2-phenylethane, B 1-triethoxysilyl-1-phenylethane. <sup>b</sup> For calculation see Experimental. <sup>c</sup> The *k*<sub>rel</sub>'s increased with increasing content of 1-heptyltrichlorosilane in its mixture with the internal isomer (see Discussion). The values listed in the table were determined from experiments in which its content was 60 ± 5%. <sup>d</sup> The catalyst was little active. The reason is not yet clear.

## EXPERIMENTAL

*Preparation of catalysts.* A series of macroreticular styrene-divinylbenzene copolymers supplied by the Research Institute of Synthetic Lacquers and Resins, Pardubice, was used as supports. The degree of cross-linking was controlled by the percentage of the divinylbenzene used in the production of the polymer. We used the following polymers (the portion of divinylbenzene is given in parenthesis): P<sub>1</sub> (10% DVB), P<sub>2</sub> (15% DVB), P<sub>3</sub> (25% DVB), P<sub>4</sub> (40% DVB), P<sub>5</sub> (50% DVB), and P<sub>6</sub> (60% DVB) (Table I). These compounds were chloromethylated<sup>8</sup> and then reacted with dimethylamine<sup>8</sup>, yielding the polymers containing dimethylamino groups (DAMS). Polymer-supported rhodium catalysts were obtained in the following way: To 10 g of DAMS in 200 ml of benzene, 0.5 g of [(Rh(CO)<sub>2</sub>Cl]<sub>2</sub> was added under nitrogen atmosphere and the reaction mixture was refluxed for 6 h with stirring. The catalyst was filtered, washed several times with benzene and dried by freezing out *in vacuo*. The content of chlorine, nitrogen and rhodium in the catalysts prepared is given in Table I.

*Surface area determinations.* The preliminary method for determining the surface of catalysts was one-point method using air as adsorbate<sup>9</sup>. The volumetric apparatus was calibrated by ten

samples of different surfaces (varying from 10 to 250 m<sup>2</sup>/g). The specific surface area was determined by immersing the sample into a liquid nitrogen bath at the relative pressure of about 0.1, at which the amount adsorbed is proportional to the surface area. For determining the surfaces and pore-size distribution of macroreticular resins of styrene-divinylbenzene type we have already employed the sorption of n-hexane<sup>10</sup> at 20°C. Adsorption isotherms of n-hexane were measured in all-glass McBain-Bakr balance apparatus<sup>11</sup> equipped with quartz spirals. The samples (c. 0.2–0.3 g) were evacuated at 125°C for 24 h under vacuum of  $1 \cdot 10^{-3}$  Torr. n-Hexane (Lachema, Brno), freed of the isomers by means of Linde 5A molecular sieve, was distilled through a 20 TP column. Its purity was checked by g.l.c. The hydrocarbon was further dried and degassed in the way described earlier<sup>11</sup>. The surface area was calculated by BET method from five points within the region of relative pressure 0.05–0.20. The cross-sectional area of n-hexane molecule was taken as 39.4 Å<sup>2</sup>. The same procedure was used to determine the specific surface area by measuring the isotherm in the region of relative pressures 0.06–0.20 with the aid of benzene. The cross-sectional area of benzene molecule was taken as 41 Å<sup>2</sup>.

*True density* was determined by helium pycnometry. The volumes of helium, empty flask and the flask with the sample were determined under identical pressure from the loss of mercury in its reservoir. Apparent density was measured by mercury in Carlo Erba, Model 65/A, porosimeter at the pressure 760 Torr.

*Porosity.* Pore volume,  $V_S$ , was calculated from adsorbed amount of n-hexane isotherm at the relative pressure 1 according to the relation  $V_S = a_{\max} M_V / 1000 \rho$ , where  $a_{\max}$  is the amount adsorbed at the relative pressure close to 1,  $M_V$  is the molecular weight of n-hexane and  $\rho$  is the density of n-hexane at 20°C. This volume was calculated for pores of the size up to 4000 Å. Total pore volume,  $V_g$ , was calculated according to the relation  $V_g = (1/\rho_{\text{Hg}}) - (1/\rho_{\text{He}})$ . Distribution of pore-size was measured by Carlo Erba, Model 65/A mercury porosimeter for pores in the region of 75 to 75,000 Å, using the pressure ranging from 1 to 1,000 atm. Both the adsorption and the desorption branch of n-hexane isotherm were measured, using all-glass balance apparatus. The distribution curve of pores according to their size was obtained from the desorption branch of the isotherm. The calculation was carried out according to Kelvin equation

$$r_K = \frac{2\sigma M \cos \Theta}{\rho RT} \frac{1}{\ln(p_0/p)}, \quad (1)$$

where  $r_K$  is Kelvin pores radius,  $\sigma$  is the surface tension of n-hexane,  $\Theta$  is wetting angle,  $\rho$  is the density of n-hexane,  $R$  is the gas constant,  $T$  is Kelvin temperature,  $p_0$  is the pressure of saturated vapours, and  $p$  is the equilibrium pressure. The measurements were carried out at 293°K. At this temperature  $p_0 = 120$  Torr.

*Dispersion of the metal on catalyst surface* was followed by the chromatographic method worked out by Bujanova and coworkers<sup>12</sup>. A sample of the catalyst was purged with a stream of hydrogen-helium mixture (total flow rate was 33 ml/min,  $p_{\text{H}_2}$  was 0.75 at) at room temperature for 1 h, then at 57°C for 1 h, at 93°C for 2 h, and finally at 140°C for 1 h. The catalyst was then reduced by a stream of hydrogen (30 ml/min flow rate) at 140°C for 16 h, washed with a stream of helium for 45 min and cooled under helium atmosphere to room temperature. Oxygen pulses (0.220 ml) were introduced in 100 s intervals, each dose lasting 15 s. Sample loop was calibrated by mercury. The calibration of dead space of sampling cock<sup>13</sup> was made by means of several loops with the known volume. The flow rate of oxygen through the loop was 30–40 ml/s, the helium flow rate was changed from 10 to 50 ml/s. In this way a linear calibration graph was obtained. The negative intercept on the abscissa corresponded to the value of the feed volume in the sampling cock.

In the titration of reduced catalysts with oxygen the amount of oxygen adsorbed on the catalyst was calculated as the sum of the volumes of the peaks of oxygen which disappeared and those which did not correspond to the total charge of the oxygen. The weighed amount of the catalyst was about 0.2 g. The surface area of the metallic portion of the catalyst was calculated according to the expression  $S = (N\sigma/M)R$ , where  $S$  denotes the surface area,  $N$  is Avogadro number, and  $M$  is the atomic weight of rhodium. The effective size area of rhodium atom  $\sigma$  was calculated as the average of the three crystallographic planes (100), (110), and (111) and equaled to  $8.4 \text{ \AA}^2$ .  $R$  is the proportion of rhodium atoms on the surface relative to the total amount of rhodium atoms in the catalyst. This quantity can be calculated providing that the number of oxygen atoms per one rhodium atom in the titration of the surface by oxygen is known. In our case one oxygen atom is supposed to be consumed in the reaction with hydrogen (which was irreversibly bound to the surface after the reduction) and only the second oxygen atom adsorbs on rhodium atom and forms a new layer on the surface.  $R$  is therefore defined by the  $O_2/\text{Rh}$  ratio. This type of the sorption of oxygen on rhodium at  $0^\circ\text{C}$  was already reported<sup>14</sup>. The average length of crystallite edge  $d$  was calculated from the specific surface of rhodium  $S$  according to the expression  $d = (5/S\rho)$ , where  $\rho$  is the density of the metal.

*Substrates and procedure.* The hydrocarbons used in activity and selectivity tests (1-heptene, styrene, 3,3-dimethyl-1-butene, and 4,4-dimethyl-1-pentene) were supplied by Fluka AG, Buchs, (Switzerland), except butadiene (>98%), which was of inland production (Kaučuk, Kralupy/Vlt.). Trichlorosilane, triethylsilane and triethoxysilane were from laboratory stock. Their purity was checked by g.l.c. All the compounds were degassed, stored in Schlenk tubes under nitrogen, and used without further purification, except butadiene which was dried as liquid over molecular sieve. All the operations with reactants and catalysts were carried out with the exclusion of air, using a vacuum line. The reactions took place in sealed glass ampoules in the absence of solvent under conditions specified later. In each of the reactions tested polymer catalysts were used in such amounts as to ensure practically the same concentration of the metal in all runs. In addition, parallel tests with the precursor of catalysts, tetracarbonyldichlorodirhodium, and a soluble model rhodium catalyst, prepared *in situ* from the rhodiumcarbonylchloride and benzyl-dimethylamine (in the 1 : 2 molar ratio), were carried out under identical concentration and experimental conditions with those used with polymer-supported catalysts.

*Activity of the catalysts* was tested by the reaction of trichlorosilane with 1-heptene. In a typical experiment, a mixture of 8.8 mg of the catalyst P3, 0.5 ml (3.5 mmol) of 1-heptene and 0.35 ml (3.5 mmol) of trichlorosilane was heated in a sealed glass ampoule under nitrogen at  $100^\circ\text{C}$  for 2 h and the composition of the reaction mixture was analysed by g.l.c. (3 m — column filled with 16% Trifluoro Propyl Methyl Silicone FS 1 (Pye, England) on 30–60 mesh Chromosorb W;  $150^\circ\text{C}$  oven temperature, 30 ml/min nitrogen flow rate. 1-Heptyltrichlorosilane prepared in separate experiment was used as standard).

*Selectivity measurements* concerned three reactions: hydrosilylation of styrene by trichlorosilane ( $100^\circ\text{C}$ , 2 h) and triethoxysilane ( $80^\circ\text{C}$ , 2 h), the addition of triethoxysilane to 1,3-butadiene ( $100^\circ\text{C}$ , 4 h), and competitive hydrosilylation of 3,3-dimethyl-1-butene and 4,4-dimethyl-1-pentene by triethylsilane ( $50^\circ\text{C}$ , 2 h), using 1-heptene as reference olefin. Except the last reaction, all the experiments were performed in the way similar to that described in the preceding paragraph, with practically equimolar amounts of the reactants. The composition of resulting reaction mixtures was analysed by g.l.c. (Chrom 3 chromatograph, Laboratorní přístroje, Prague) under the following conditions: styrene + trichlorosilane — a column (3 m) filled with the Silicone FS1 (16%) on Chromosorb W (30–60 mesh),  $190^\circ\text{C}$  oven temperature, 30 ml per min nitrogen flow rate, 1-trichlorosilyl-1-phenyl- and 1-trichlorosilyl-2-phenylethane used as standards were prepared by chloroplatinic acid-catalysed reaction; styrene + triethoxysilane and butadiene + tri-

ethoxysilane — 1.5 m-column filled with 10% ICI Silicone Elastomer E 302 on Chromaton, 50—170°C oven temperature (speed 6°C per min), 30 ml/min hydrogen flow rate, the reaction products (1-triethoxysilyl-1-phenyl- and 2-phenylethane and *cis*- and *trans*-2-butenyltriethoxysilane) were identified by comparing their retention times with those of authentic samples prepared earlier in this laboratory<sup>15</sup> and characterized by elemental analysis, IR and NMR spectroscopy.

*Competition experiments* were carried out under the reaction conditions which ensured the necessary low conversion of the olefins. As an example, a mixture of 14.7 mg of the catalyst P<sub>2</sub>, 0.339 g (3.5 mmol) of 1-heptene, 0.225 g (3.7 mmol) of 3,3-dimethylbutene, and 0.1 ml (0.6 mmol) of triethylsilane was heated in sealed glass ampoule at 50°C for 2 h, and the reaction mixture was analysed by g.l.c. (for the conditions see the butadiene + triethoxysilane reaction). Relative rate constants were calculated according to the relation  $k_{rel} = (A_0/A_{std})(I_{std}/I_0)$  where  $I_0$  and  $I_{std}$  are weighed amounts of the olefin whose relative reactivity is to be determined and of 1-heptene, respectively, and  $A_0$  and  $A_{std}$  are the chromatographic peak areas for the products formed from each. The use of this simplified relation was made possible by similar molecular weights of the starting olefins and of the products as well as by the response factor<sup>16</sup> for the products equaling to 1. The results of the experiments are listed in Table I.

## RESULTS AND DISCUSSION

### *Texture Changes During Synthesis of Catalysts*

In polymer-analogous reactions the surface and texture changes observed are caused by several factors<sup>17</sup>, and that both by mass increase on the surface of pores, and by change in polarity of the surface, which brings about the change in their medium radius, *i.e.* in our case by introduction of functional groups which are to serve to the formation of ligands capable of coordination to the metal, and, finally, also by further cross-linking of the polymer matrix. As shown in Table I, with increasing content of DVB increases also the magnitude of nitrogen surface of the basic copolymer and of the copolymer chemically modified by chloromethylation, by introduction of dimethylamine group and by formation of rhodium coordination bond. The surface area of the catalyst P<sub>6</sub> is nearly ten times as great as that of P<sub>1</sub> in all cases. The surfaces increase markedly when going from P<sub>1</sub> to P<sub>3</sub>; the differences between P<sub>4</sub> and P<sub>6</sub> are not so great. With copolymer P<sub>1</sub>, the surface area increases during chemical treatment so that the area of the rhodium catalyst is doubled, relative to the starting substance not containing functional groups. In the case of P<sub>3</sub> and P<sub>4</sub> the surface areas do not undergo so marked changes during chemical treatment. This may be due to the fact that by the effect of amine and the ligand formed there proceeds filling up of a part of micropores and additional cross-linking. As the result, the pores of greater diameter are formed by formation of new surface roughness, edges and cracks. This phenomenon does not affect the surface area and results only in formation of the greater number of pores of radii greater than 300 Å which are important with regard to the course of chemical reaction (Table I). During chloromethylation surface areas of catalysts P<sub>2</sub> — P<sub>5</sub> decrease, which may be due to the

filling up of the pores in the course of the reaction. The original texture reappears again in the rhodium catalyst, since the pores of the radii 20 and 100 Å are preserved and were already observed in the unsubstituted  $P_3$ <sup>10</sup>. In the cited work it was also reported that in the original polymer  $P_3$  ( $P_3 = S$ ) the total volume of the pores is by 50 per cent and the volume of pores from 75 to 75000 Å is by 150 per cent smaller than in the rhodium catalyst  $P_3$ , which should have been caused by the formation of the greater pores during synthesis of the catalyst. Polymer  $P_6$  preserves its surface characteristics during chemical transformations due to its high cross-linking, except formation of macropores.

With the aim to compare surface areas of the rhodium catalyst, we measured benzene and n-hexane isotherms, the last being also used to determine distribution of pores according to their size<sup>10,11</sup>. We wished to study their texture and, at the same time, to confirm the same increase in the surface area along the series  $P_1 - P_6$  as we obtained by surface area measurements with the use of one-point method. Also in this case the surface area of  $P_6$  was four times larger than that of  $P_1$ . Similarly, the pore volume of  $P_6$ , determined by n-hexane adsorption, was four times greater, compared with  $P_1$ . In the case of  $P_1$  the pore volume is nearly the same as the total volume of all pores, which indicates the absence of macropores in this catalyst. This is also obvious from the distribution of pores, both from n-hexane isotherm, and from mercury porosimetry, since distinct maxima appear for micropores and pores around 100 Å; that we deal here with the pores smaller than 75 Å is evident also from the value of pore volume obtained by porosimetry which is by 15 per cent smaller than the value of total pore volume.

Similarly, nearly the same values of the total pore volume were determined by all the methods used for  $P_2$ ; again, macropores are not present. Also the maximum of the occurrence of the pores lies in the region of micropores and the 260 Å pores. Relative occurrence of micropores and the pores smaller than 75 Å is here greater than that of intermediate pores and is ten times greater than in  $P_1$ . The portion of micropores and intermediate pores in the rhodium catalysts  $P_3 - P_6$  remains the same. Starting from  $P_3$ , there appear macropores, as discussed earlier, and their proportion increases with increasing degree of cross-linking of the catalyst. At the same time, total pore volume increased, too. The volume of pores within the region of 75–75000 Å is also greater than that of the pores to 4000 Å, which confirms the existence of the greater proportion of macropores on distribution curves. The volume of pores in  $P_5$  and  $P_6$  is comparable in value; only the occurrence of macropores in  $P_6$  is slightly higher whereas pores of radii under 300 Å are not so frequent as it is in  $P_5$ . The region of macropores decisive for transport phenomena and important with regard to the course of catalytic reaction is thus quite evident. When comparing the results of the reaction of trichlorosilane with 1-heptene and styrene with the pore size distribution of intermediate pores and macropores (Table I), the activity and the frequency of larger pores occurrence is rising simultaneously on going from  $P_1$  to  $P_6$ . The first

two catalysts have the negligible amount of larger pores and no catalytic reaction is taking place. At forty and fifty per cent of pores larger than 300 Å the catalysts become active ( $P_3$  and  $P_4$ ). The highest activity was found with  $P_6$ , which was especially in the reaction with styrene much higher than with  $P_5$ , whereas the difference in larger pore occurrence is not so pronounced. However, as the pore size distribution is not the only factor influencing the activity, this relation cannot be evaluated quantitatively.

With the aim to study the action of organometallic complex, we decided to reduce the catalyst in such a way which would enable us to examine the effect of different degree of cross-linking of the polymer on dispersion of the metal residing on the surface, *i.e.* on the specific surface of the metal itself. In a dynamic system fast irreversible sorption of oxygen should occur on the surface of the catalyst and that is why pulse chromatographic methods are employed with advantage in the study of supported metal catalysts<sup>12,13</sup>. Slow chemisorption as well as physical sorption should not play a role under such conditions. The sorption of oxygen on rhodium metal has already been reported in the literature<sup>12</sup>. After finding suitable conditions for reduction of the complex to the metal, assuming complete reduction only when the amount of oxygen adsorbed was not increasing any more, we titrated in the same way DAMS ( $P_1$  and  $P_6$ ) without the rhodium complex. The sorption of oxygen did not occur. The O/Rh ratio and the specific surface area of the rhodium calculated from this ratio, found for complex bonded and reduced polymers are listed in Table I. In the case of  $P_5$  and  $P_6$  rhodium was completely dispersed on the surface as crystallites with the length of edges equaling to 14 and 15 Å, respectively. X-ray showed no lines of Rh on  $P_5$  or  $P_6$ . The specific surface area is formed here essentially by the surface of the metallic component. The lower dispersion ratio observed with catalysts  $P_1 - P_3$  may result either from inaccessibility of rhodium complexes in narrow pores, or from aggregation of the metallic rhodium after the reduction.

In conclusion, a great difference between the texture of  $P_1$  and that of the other polymers is worthy of note. At 10% cross-linking of the styrene skeleton by divinylbenzene, the surface of the catalyst and the volume of its pores are distinctly smaller than in the case of the more cross-linked catalysts. Also there are no pores greater than 130 Å. The polymers with 25 and 40% cross-linking have larger surface area and the greater amount of intermediate pores and macropores which were formed during chemical treatment of the support, which demonstrates itself in the greater volume of the pores greater than 75 Å and in the greater proportion of these pores on distribution curve. The most cross-linked catalysts  $P_5$  and  $P_6$ , with the largest surface and the greatest amount of transient pores and macropores, should be most active. The same conclusions were reached also on the basis of titration of the reduced catalyst by oxygen.



*Activity and Selectivity of the Rhodium Catalysts in Hydrosilylation*

In order to verify the conclusions drawn from the measurements of the texture of the catalysts, we first followed the changes in their activity, using the reaction of trichlorosilane with 1-heptene as model reaction. This reaction was chosen on the basis of preliminary experiments which showed a marked change of the activity along the series of the catalysts studied. With other silanes tested, such as triethylsilane and triethoxysilane, the reaction proceeded smoothly already under relatively mild conditions (50°C, 2 h) with all the catalysts, giving high yields of the products, 1-heptyltriethylsilane and 1-heptyltriethoxysilane, respectively. The high reactivity of these silanes has been utilized in the selectivity measurements (see below). From the results listed in Table I it is seen that the conversions change over a wide range. The increase in the yields of 1-heptyltrichlorosilane along the series P<sub>1</sub> – P<sub>6</sub> roughly parallels the increase in the surface areas of these catalysts, lending thus support for the assumption made on the basis of texture measurements. A similar trend in the activity of the catalysts was also observed in hydrosilylation of styrene with trichlorosilane. Here, the reaction was non-selective, giving with catalysts P<sub>5</sub> and P<sub>6</sub> a mixture of the two isomers, 1-phenyl-1-trichlorosilane and 1-phenyl-2-trichlorosilane in c. 1 : 2 molar ratio. The yields listed in Table I were calculated as overall yields of both products. Compared with the chloroplatinic acid-catalysed reaction<sup>14,18</sup>, rhodium catalysts thus prefer the formation of the terminal isomer. Besides the different electronic structure of the complex this may be also due to the possibility that the coordination of the metal to a polymeric support changes its steric environment (by attachment of bulky ligand), so that in terms of the mechanism of hydrosilylation catalysed by rhodium complexes suggested by Chalk<sup>19</sup>, transient formation of n-alkyl-rhodium bond is favoured over the formation of isoalkyl-rhodium bond. With the aim to obtain information concerning the role of polymeric ligand we attempted at carrying out this hydrosilylation in the presence of the soluble rhodium complex used to prepare the polymer catalysts, tetracarbonyldichlorodirhodium, and of a mixture of this complex and benzyldimethylamine (1 : 2 molar ratio) (see Experimental). Unfortunately, in both cases, instead of hydrosilylation, rapid polymerization of styrene took place already during the preparation of the reaction mixtures.

As in the trichlorosilane + styrene reaction catalysts P<sub>1</sub> – P<sub>4</sub> turned out to be inactive or little active, we carried out this reaction with the more reactive triethoxysilane. Here, the formation of the 2-silyl-substituted derivative was slightly favoured on all the catalysts. The molar ratios of the 2-silyl- to the 1-silyl-substituted product changed in a non-systematic fashion, without distinct dependence on texture properties of the catalysts (Table I). A similar ratio was also obtained on catalysing the reaction with a mixture of the rhodium-carbonyl complex and benzyldimethylamine (1 : 2 molar ratio) under identical conditions (1.6, the average of three measurements).

Our continuing interest in hydrosilylation of conjugated dienes<sup>20</sup> led us to examine the effectiveness and selectivity of the rhodium catalysts also in the addition of triethoxysilane to butadiene, the reaction which in general may yield several types of products (a bis-triethoxysilyl-substituted butane, 1-triethoxysilyl-2-butene or -3-butene, or, eventually, also an octadienyltriethoxysilane). Under the experimental conditions chosen (100°C, 4 h), high conversions of triethoxysilane were obtained with all the catalysts (80–95%, by g.l.c.). The reaction was highly selective, giving in all cases the *trans*- and the *cis*-2-butenyltriethoxysilane as major products, with thermodynamically favoured *trans*-isomer prevailing (Table I). The other products, formed only in small amounts (c. 3–5 per cent each), were identified with 1,4-bis(triethoxysilyl)butane and vinylcyclohexene (by g.l.c.). Practically the same result was obtained with the soluble rhodium complex (almost quantitative conversion of triethoxysilane, the mixture of the 2-butenylsilanes contained 82.5% of the *trans*-isomer).

We further attempted to estimate the selectivity of the rhodium catalysts by determining relative rate constants of hydrosilylation of 3,3-dimethyl-1-butene and 4,4-dimethyl-1-pentene with triethylsilane by the method of competitive reactions, using 1-heptene as a reference compound. The reaction had an unexpected course, giving in the former case a mixture of the three and in the latter of the four hydrosilylation products. In both cases the two of them were terminal silyl-substituted alkanes, 1-heptyltriethylsilane and (3,3-dimethyl-1-butyl)triethylsilane (resp. (4,4-dimethyl-1-pentyl) triethylsilane). The others were found by mass spectrometry to have the same molecular weight as the corresponding terminal products. The elemental analysis of both products arising from individual olefins also indicated that we deal here with a mixture of isomers. Furthermore, the IR spectra of the mixture showed no absorption band in the 2100–2200 cm<sup>-1</sup> region, corresponding to the Si–H stretching vibration. This excludes the possibility that these compounds are the products of the addition of diethylsilane, arising from rhodium catalysed disproportionation of triethylsilane. As to the structure of hydrosilylation products from 4,4-dimethyl-1-pentene, its possible skeletal isomerisation, followed by the addition of the hydride, should also be considered. We made therefore several experiments aimed at evaluating the extent of this reaction under the conditions employed in competitive hydrosilylations. We found that in the absence of the silicon hydride the olefin was isomerized to two isomers (4% of each, by GLC), GLC retention time of one of which was identical with that of 4,4-dimethyl-2-pentene. The low conversion of the reaction prevented us to determine the structure of the other isomer by IR spectroscopy. Both isomers (again in comparable amounts) were also formed to nearly the same extent (6% of each, by GLC) in the presence of triethylsilane. On the basis of these facts it is reasonable to assume that the unexpected products found in competitive hydrosilylations are corresponding nonterminal isomers. To our knowledge, this would be the first example of their formation from simple olefins in the rhodium catalysed hydrosilylation. As found by separate experiments with single olefins, the

formation of these adducts occurred only when the olefin was used in large excess with respect to the silane (as required in competitive experiments). Two hydrosilylation products were not formed when the reaction was carried out with equimolar amounts of the reactants. In the case of 3,3-dimethyl-1-butene, the reaction led only to terminal product even when the olefin was used in excess. The same situation arose also when the soluble rhodium carbonyl chloride was used as catalyst. The fact that Markovnikoff adduct was not observed with 3,3-dimethyl-1-butene is not surprising, since here the internal carbon of the double bond is sterically screened by adjacent tert-butyl group, which makes its attack by bulky triethylsilyl group much less probable. The relative rate constants, listed in Table I, show again no significant dependence on the texture of the catalysts and are comparable with the values obtained with tetracarbonyldichlorodirrhodium ( $k_{rel}$  for the first reaction was 0.82, for the second one 0.21).

As to the function of the catalysts, the results so far obtained provide no conclusive information. The increase of the activity with increasing surface area of the catalysts, along with their similar selectivity, may be explained in two ways. Either the reaction takes place in pores of the catalyst which are so "open" that they impose no steric demands on the reactants, the activity changes being then the result of different rates of diffusion of the reactants to active sites of individual catalysts, or the polymer-supported complex acts only as precursor of soluble catalytically active species, the reaction proper is taking place in solution, the activity being dependent on the ease with which this species, presumably an olefinic rhodium complex, is abstracted from the polymer support. Both of these possibilities were, in fact, reported to occur with complex polymeric catalysts<sup>3,21</sup>. In preliminary experiments we found that a part of the metal is transferred from the polymer to the solution during the reaction (e.g. 40% in the reaction of triethylsilane with 1-heptene catalysed with  $P_2$ , as determined by absorption spectrometry of the solution after the removal of the polymer catalyst). Relative importance of the above processes is the subject of further study in this laboratory.

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