CATALYSTS AND BIOCATALYSTS ANCHORED TO INORGANIC SUPPORTS

Martin ČAPKA

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol

Received May 16, 1990
Accepted June 13, 1990

The review deals with transition metal complexes and enzymes chemically bonded to inorganic supports by means of silyl-substituted anchoring ligands. The synthesis of these functionalization agents, the effect of immobilization procedure, the length of spacer, the texture of support and the structure of anchoring ligand are mentioned. Conclusions based on kinetic studies of the efficiency and selectivity of immobilized catalysts in hydrogenation, hydrosilylation, isomerization, polymerization and enzymatic reactions are discussed. Proposed mechanisms of the action of these catalysts are supported by the results of IR, NMR, ESCA and ESR studies. The attention is paid to the leaching and deactivation of catalysts, to the other types of immobilized catalysts such as those anchored via polymer ligands or via ligands in molten phase as well as to the effect of support texture and particle shape, to prepare the catalysts with limited nonspecific sorptions and long lifetime.

1. INTRODUCTION

After the year 1835, when Berzelius introduced the concept of catalysis, catalytic processes had soon been divided into homogeneous, i.e. those in which all the reactants and catalysts taking part in the reaction are in one (usually liquid) phase and heterogeneous ones in which the catalyst is solid and the reactants are in gaseous or liquid phase. Both types of catalysis mentioned show some advantages and at some time also disadvantages in their application. As far as the homogeneous catalysts are concerned (usually those based on metal complexes or enzymes), they exhibit high selectivity and activity at relatively low temperatures, but their separation from the products is generally difficult. This fact limits significantly their applicability, since with expensive metals the economy of the process is endangered. In the case of the free enzymes, a number of products become unsalable as at present the presence of artifical substances in the food is forbidden. Finally, the heterogeneous catalysts possess usually good lifetime and can be easily separated from the reaction mixture but are much less selective and frequently active only at high temperatures.

The idea of combining the advantages of both types of catalysts had become thus attractive and the great effort has been spent in its realization. The first successful type of heterogenized catalysts were the ion exchangers commercionalized after the Second World War and since then widely applied in acid-base catalysis. In the sixties the first examples of immobilized enzymes were reported and in the seventies the heterogenized transition metal complexes became to be developed and increasingly studied. However, the most of the immobilized compounds have so far been bonded to organic polymers[1-11], regardless of the advantages of inorganic supports.

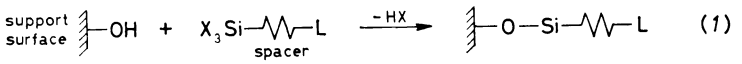
In general, a support suitable for immobilization should have appropriate texture, sufficient surface and pore volume, optimal particle size, good mechanical properties, as well as the resistance toward solvents, higher temperatures, microbial attack, etc.

These requirements are well fulfilled by a number of readily available cheap commercial inorganic materials. The most frequently used silicon dioxide (silica) offers choice of very different pore size, surface and shape of particles and it is also relatively cheap. Its greatest disadvantage is broad pore distribution. Even the so called wide-pore silica (defined as such usually based only on pore volume) contains substantial amount of micropores which form thus the main part of specific surface. On the other hand, as far as pore size distribution is concerned, an "ideal" material is porous glass in which the mean pore diameters determined from surface and from volume are nearly identical; its disadvantage is especially the high price and the lower mechanic stability. The ceramics with controlled pore size is also financially little acceptable. However, in some applications (especially on large scale) one can use cheap, common ceramic materials after their appropriate treatment, such as ground porous tiles, shaped brick and like. As unsuitable for immobilizations have

turned out to be zeolites which possess too small cavities, the ground quartz with minimal number of hydroxyl groups and the aluminas, the strong acid-base sites of which usually interfere in catalysed process. The survey of common inorganic materials is presented in Table I.

However, up to now, nonporous supports with only external surface have been unjustly neglected. The main advantage of these materials is the absence of internal diffusion and supressed nonspecific physical sorptions. As their surface is inversely proportional to their particle size, one should use micron or submicron particles. This makes their application in columns impossible. Nevertheless, they can be applied with success in batch processes especially when relatively low concentration of the immobilized substance on the support (by order of 10^{-9} mole per g) is sufficient.

For purposes of catalyst or enzyme immobilization, common inorganic supports do not possess suitable groups which would act as anchoring ligands and thus they should be functionalized by the reaction of carbofunctional silanes with free surface hydroxyl groups of a given support. This is schematically depicted in Eq. (*1*),



(*1*)

where X is chloro or alkoxy group, spacer is the chain separating both functions, and L stands for monodentate or bidentate anchoring ligand (in the present work espe-

TABLE I
Common industrial inorganic supports

Support	Surface m^2/g	Mean pore diameter, nm	Graining
Silica	20—500	2—200	5 μm—1 mm
Porous glass	30—300	1—200	0·1 mm—1 mm
Alumina	50—200	3—15	10 μm—1 mm
Zeolites	100—500	0·5—1	10 μm—5 mm
Ceramics	1—300	5—50	0·1 mm—1 mm
Ground quartz	ca 1	[a]	ca 1 μm
Aerosil	50—300	[a]	ca 0·01 μm
Glass balls	10^{-1}—10^{-3}	[a]	10 μm—1 mm

[a] External surface.

cially amine, phosphine, epoxy, cyano, alkene, cyclopentadienyl, ammonium, and sulphonic acid groups).

The so treated supports are then used in immobilization. However, there are alternative routes to anchored transition metal complexes or enzymes. These involve the preformation of the complex of transition metal with the functionalization agent or the use of the polymer ligand adsorbed on support.

However, the synthesis of the support and immobilization of the complex do not solve all the problems. The behaviour of the immobilized catalyst is affected by a number of effects – i.e. by the texture of the support, the kind of the bond between the complex and the support, the type of the complex, and the structure of the reactants. These factors all determine the availability, activity, selectivity and performance of immobilized catalysts.

At the beginning of our studies, the question of proper choice of anchoring ligand, immobilization procedure, suitable transition metal and some other problems were solved empirically (cf. refs[1-3]). Although the results of these exploratory studies had been promissing, the catalysts[1-3] of this type were imperfect from standpoint of their wider application; they suffered from metal leaching, were prone to deactivation, and also their activity and selectivity was low.

To overcome these deficiencies we centered on the following problems: (i) development of methods for functionalication of inorganic supports which for purposes of immobilization would compare well with the earlier used organic supports, (ii) efficient ways of supressing metal leaching, (iii) enhancement of the activity of complexes of cheaper metals, enabling their substitution for platinum metals in some catalytic processes, and (iv) investigation of the conditions under which the immobilized complex would exhibit higher activity compared to the soluble analogue.

We believed that solution of at least some of the above problems would contribute not only to the knowledge of immobilized catalysts but also to their wider application, especially in the field of special chemical products.

2. SYNTHESIS OF FUNCTIONALIZED SUPPORTS

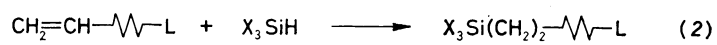
There are two ways of functionalization of inorganic suports: *a*) according tc Eq. (*1*), i.e. by one-step treatment of the support with silyl-substituted anchoring ligands, and *b*) by multistep, stepwise formation of the spacer and of the anchoring ligand on the support surface by polymer-analogous reactions, similarly to the synthesis of some functionalized organic polymers.

The synthesis depicted in Eq. (*1*) requires the availability of silyl-substituted anchoring ligands. Some of them (especially these containing primary amino groups, cyano, vinyl or epoxy groups) are already commercial products, because of their industrial application as coupling agents in composite materials, especially filled organic polymers[12]. Although they can be used in some enzyme immobilizations,

for anchoring of transition metal complexes they are unsuitable. This led us to work out methods for the synthesis of novel anchoring agents containing monodentate or bidentate phosphine groups or cyclopentadienyls.

2.1. *Synthesis of Silyl-Substituted Ligands by Hydrosilylation*

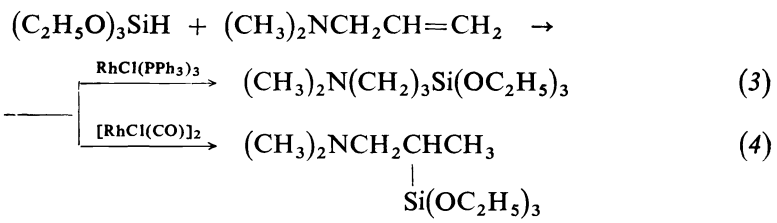
Providing that one can easily synthesize the ligand containing alkenyl group and that the ligand proper does not act as catalytic poison, the title organofunctional silicon compounds can be obtained by hydrosilylation (Eq. (*2*)).



$$CH_2{=}CH{-}\sim{-}L + X_3SiH \longrightarrow X_3Si(CH_2)_2{-}\sim{-}L \qquad (2)$$

This route has been used for preparing ligands of several types. Thus, for example, hydrosilylation[13] of 5-(dimethylamino)-1-pentene by triethoxysilane in the presence of Wilkinson catalyst ($RhCl[PPh_3]_3$) yielded 5-(dimethylamino)pentyltriethoxysilane. When the starting substance contains more C=C bonds, like conjugated dienes, hydrosilylation to the first stage affords silyl-substituted alkenyl ligands, as demonstrated by series of alkenyltriethoxysilanes obtained by hydrosilylation of 1,3-butadiene, 2-methyl-1,3-butadiene or vinylcyclohexene[14].

Hydrosilylation of allylamine, reported earlier as nonselective, can, as found by us, be controlled by choice of the catalyst, giving desired isomer in high yield[15] (Eqs (*3*) and (*4*)). Especially regioselective formation of the Markovnikow



$$(C_2H_5O)_3SiH + (CH_3)_2NCH_2CH{=}CH_2 \rightarrow$$

$$\xrightarrow{RhCl(PPh_3)_3} (CH_3)_2N(CH_2)_3Si(OC_2H_5)_3 \qquad (3)$$

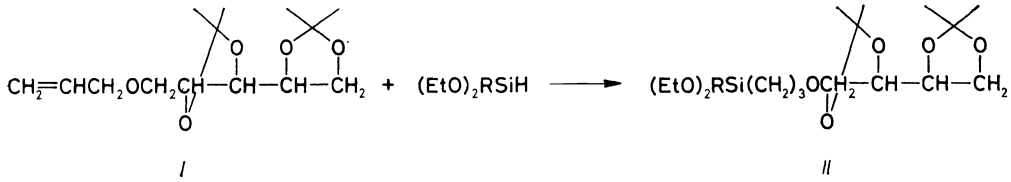
$$\xrightarrow{[RhCl(CO)]_2} (CH_3)_2NCH_2\underset{\displaystyle Si(OC_2H_5)_3}{\underset{|}{C}}HCH_3 \qquad (4)$$

adduct (Eq. (*4*)) deserves special mentioning as till that time hydrosilylations were known to obey generally anti-Markovnikow rule[16,17].

Such case is hydrosilylation of allyl phenyl ether by trichlorosilane where by use of H_2PtCl_6–Ph_2SiH_2 system substantial increase (by more than 30 per cent) of the yield of anti-Markovnikow adduct, (3-phenoxypropyl)trichlorosilane, had been further achieved[18]. This product is the important starting compound for synthesis of inorganic cation exchangers[19].

On the other hand, hydrosilylation of 3-(dimethylamino)-1-propyne was found to be nonselective[20], similarly to that of phenylacetylene[21] which in the presence of rhodium complexes reacted with series of chloro- and alkoxysilanes to give a mixture containing both position (1- and 2-silylsubstituted styrenes) and geometrical

((*E*)-, (*Z*)-) isomers. Hydrosilylation of the allyl group in 1-O-allyl-2,3 : 4,5-di-O-isopropylidene-D-arabitol (*I*) by triethoxysilane and methyldiethoxysilane afforded[22] the corresponding silyl-substituted arabitols (*II*, R = Me or EtO) as one of the first examples of chiral organosilicon functionalization agents.



I *II*

2.2. *Synthesis of Silyl-Substituted Ligands by Nucleophilic Substitution of (Halogenoalkyl)alkoxysilanes*

Compared to the ligands mentioned in the preceding chapter, for immobilization of transition metal complexes, the more important anchoring ligands are undoubtly those containing phosphinyl groups. However, these agents cannot be prepared by hydrosilylation of the corresponding alkenylphosphines, as in the presence of such a phosphine in excess, hydrosilylation catalyst becomes inactivated.

The only silyl-substituted phosphine, (2-triethoxysilyl)ethyldiphenylphosphine, earlier reported[23] had been prepared by hydrophosphylation of vinyltriethoxysilane (CH_2=$CHSi(OEt)_3$) with diphenylphosphine (Ph_2PH).

Therefore, we worked out novel procedure for synthesis of silyl-substituted phosphines[24–26] based on the nucleophilic substitution of the halogen of ω-(halogenoalkyl)triethoxysilane with the use of alkali metal diphenylphosphide (Eq. (*5*), where X = Cl, Br; n = 1, 3–6).

$$Ph_2PLi + X(CH_2)_nSi(OEt)_3 \rightarrow Ph_2P(CH_2)_nSi(OEt)_3 \qquad (5)$$

It is of interest to note that under conditions used, the nucleophilic attack takes place at carbon and not at silicon as could have been expected by analogy[27] with Eq. (*6*).

$$Si(OEt)_4 + nRLi \rightarrow R_nSi(OEt)_{4-n} \qquad (6)$$

This method was used with success in preparing chiral alkoxysilylsubstituted phosphines. The nucleophiles were both lithium phenylmenthylphosphide[24] and alkali metal dimenthylphosphide[26]. Also prepared by this way were ω-(methyldiethoxysilyl)alkyldiphenylphosphines[25] as well as their dimethylethoxysilyl[25] and trimethylsilyl analogues[28].

Of great importance is synthesis of the triethoxysilyl-substituted bidentate phos-

phines[29] (depicted in Scheme 1) which along with a silyl-substituted DIOP (ref.[30]) are still the only examples of the ligands of this type.

$$Ph_2PCH_2CH_2P(Ph)H \xrightarrow{K} Ph_2PCH_2CH_2P(Ph)K$$
$$\xrightarrow{(EtO)_3Si(CH_2)_nX} (EtO)_3Si(CH_2)_nP(Ph)CH_2CH_2PPh_2$$
$$Ph_2PCH_2CH_2PPh_2 \xrightarrow{Li} Ph_2PCH_2CH_2P(Ph)Li$$
$$n = 1, X = Cl \quad n = 3, X = Br$$

SCHEME 1

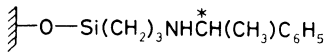
The catalysts anchored by means of these ligands showed good catalytic properties[29] and the method of nucleophilic substitution of the silyl-substituted alkyl halogenides proved to be valuable in the synthesis of organofunctional silanes. Its application was extended also to the other strong nucleophile – alkali metal cyclopentadienide[31] (Eqs (7) and (8)).

$$2\,C_5H_6 + 2\,Na \rightarrow 1\,C_5H_5Na + H_2 \qquad (7)$$

$$(EtO)_3Si(CH_2)_nCl + C_5H_5Na \rightarrow (EtO)_3Si(CH_2)_nC_5H_5 + NaCl$$
$$n = 1, 3 \qquad (8)$$

Whereas the reaction (7) was already known, the reaction (8) had not been reported. We found that under specific reaction conditions (−30°C, perfect stirring, slow addition of the cyclopentadienide) the reaction (8) is even sufficiently selective, giving the desired products in 58 and 66% yields.

Substitution of the halogen of halogenoalkyl-substituted silanes can be effected also with the use of relatively weak nucleophiles. Thus, for example, the reaction of (3-chloropropyl)triethoxysilane or (3-bromopropyl)trimethoxysilane with readily available D-1-phenylethylamine affords[32] the optically active N-(3-trialkoxysilylpropyl)(1-phenylethyl)amines. Treatment of supports with these amines then leads to formation[33] of surface chiral centres of the type *A*.

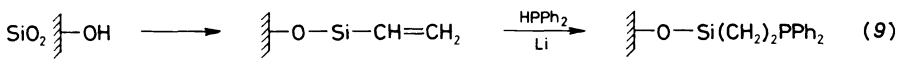


A

2.3. *Synthesis of Modifying Agents and Functionalization of Supports by Other Methods*

Although functionalization of inorganic supports by silyl-substituted ligands is very simple and in most cases also the most suitable procedure, sometimes there is no convenient way to the synthesis of suitable functionalization agent (for example the triphenylphosphine substituted at one phenyl by alkoxysilyl group has not yet

been synthesized). For that reason it seemed to be useful to pay attention also to the functionalization of inorganic supports by polymer-analogous reactions[34]. In this case we introduced first the vinyl group on the support surface which was then hydrophosphinated by the addition of diphenylphosphine catalysed by lithium (Eq. (*9*)).



(*9*)

In another case, the support was first treated with phosphorus tribromide and then with phenylmagnesium bromide (Eq. (*10*)).

(*10*)

Both methods were not, however, efficient as the catalysts bonded to these supports showed inferior properties, indicating that the above ways of surface modification are non-specific.

By contradistinction to it, we succeeded in preparing strong ion exchangers (Eq. (*11*)); the alkoxysilylpropyldimethylamines obtained by hydrosilylation were quarternized[35] by methyl iodide or by methyl tosylate, giving the corresponding ammonium salts (R = methyl, ethoxy, X iodide or sulphonate anion):

$$(EtO)_2RSi(CH_3)_3NMe_3 \xrightarrow{MeX} [(C_2H_5O)_3RSi(CH_2)_3NMe_3]^+ X^- . \quad (11)$$

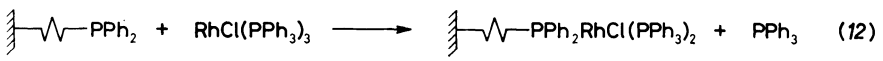
Treatment of supports with these salts yielded[36] strong inorganic anion exchanger containing chemically bonded (3-trimethylammoniopropyl)silyl group. It found use not only as the sorbent in liquid chromatography but it showed also the ability to fix ionically sulphonated tertiary arylphosphines.

The treatment of the support with carbofunctional silane followed by polymer-analogous reaction is illustrated by the following example. The silica treated with (3-phenoxypropyl)trichlorosilane obtained by hydrosilylation[18] gave the support containing chemically bonded phenoxypropyl groups. The fact that the phenyl was substituted with alkoxy group and thus activated for electrophilic substitution made the sulphonation possible under very mild conditions, preventing thus the cleavage of siloxane bonds by sulphuric acid, which otherwise is the common reaction[37]. It was synthesis of this strong cation exchanger that enabled us to get the efficient and highly selective immobilized enantioselective catalyst[38,39].

3. SYNTHESIS OF IMMOBILIZED Rh AND Ru COMPLEXES AND THEIR CATALYTIC ACTIVITY

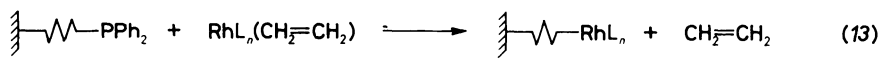
In our initial exploratory studies, rhodium complexes were fixed above all by means

of the exchange of the phosphine ligand in the soluble complex for the phosphine anchoring ligand[1-3] (Eq. (*12*)).



(*12*)

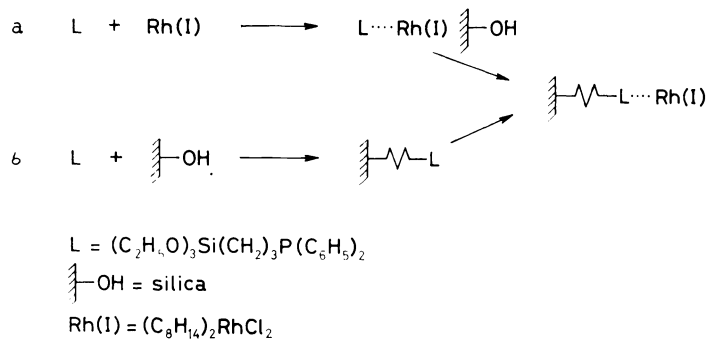
This reaction is usually equilibrium one and not always shifted to the right side. For that reason, we chose as the precursor the alkene or alkadiene rhodium complexes, the unsaturated ligands of which are readily exchanged for phosphines, e.g. Eq. (*13*).



(*13*)

3.1. *Hydrogenation*

Preparation of (3-triethoxysilylpropyl)diphenylphosphine made it possible[40] to study the effect of the immobilization procedure on the hydrogenation activity of the anchored complex (Scheme 2). This was prepared both by "traditional" way (route *b*) and also by complex pre-formation (route *a*).



SCHEME 2

As far as the route *b* is concerned, it involves the formation of the functionalized support followed by anchoring of the complex. This procedure does not ensure identical structure of surface complexes, since only sometimes anchoring ligands are located on the surface such that two phosphines can enter coordination sphere of the metal. The other ones contain likely only one anchoring ligand.

On the other hand, route *a* involes the pre-formation of the rhodium complex in situ by the reaction of the alkoxysilylated phosphine and subsequent bonding of this complex to the support. This procedure ensures obviously the uniformity of the surface catalytic centres.

A kinetic study of hydrogenation of alkenes showed that with both catalysts (including in addition also the homogeneous one), the reaction is first order in the catalyst, hydrogen and also alkene. Analogously, also the relative rate constants of the hydrogenation of alkenes catalysed by both homogeneous and heterogenized catalysts were similar[40] (Table II). This led us to conclude that in both cases the hydrogenation proceeds by the same mechanism[41,42].

When studying the dependence of the catalyst activity on the degree of surface coverage we have found[40] that at the lower degree of the coverage (0·32% Rh) it is not affected by pore size (4 or 10 nm) while at maximum coverage (0·79% Rh and 1·11% Rh) the activity of the catalysts immobilized on supports with narrow pores was markedly reduced. These findings were then utilized in preparing immobilized enzymes.

Furthermore, the heterogenized catalysts were less sensitive to deactivation processes then homogeneous ones, which was demonstrated by the greater stability of their activity. The ligand in excess has led in both heterogenized and homogeneous systems to the difficult formation of free coordination site, resulting in decrease of the reaction rate[41].

Unexpectedly, the catalysts prepared via route *b* showed higher catalytic activity compared to both homogeneous ones and those obtained by the route *b*, even though the latter route should ensure uniform centres. This result was ascribed to the dimerization and deactivation of catalytic centres and subjected to further study.

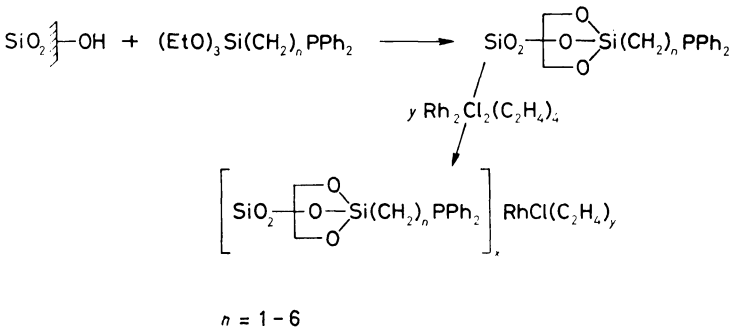
We started from the idea that the less active multinuclear surface agglomerates are formed easier when the immobilized complexes are bonded to the support surface via the longer and more mobile spacer. To verify this assumption we prepared

TABLE II
Relative rate constants of hydrogenation of alkenes

Alkene	k_{rel} for catalyst[a]	
	homogeneous	heterogenized
1-Heptene	1·00	1·30
cis-2-Heptene	0·70	0·71
trans-2-Heptene	0·17	0·42
trans-3-Heptene	0·13	0·24
Cyclohexene	0·58	0·39
α-Methylstyrene	0·93	0·93

[a] Data taken from ref.[40]; reaction conditions: $p(H_2) = 116$ kPa, 65·5°C, 10^{-2} to 10^{-1} mmol Rh, 2 ml of the alkene in 18 ml of toluene.

a series of novel (ω-trialkoxysilylalkyl)diphenylphosphines[25] differing by the length of spacer chain (from C_1 to C_6), modified silica by these ligands and immobilized then on the so treated support tetra(ethylene)-μ,μ'-dichlorodirhodium(I), as depicted in Scheme 3 (values of x and y could not be determined accurately). These complexes



SCHEME 3

turned out to be the highly active hydrogenation catalysts[25]. As follows from the rate constants presented in Table III, the most active catalysts are those in which

TABLE III

Rate constants k of hydrogenation of 1-octene catalysed by Rh(I) complexes immobilized on silica (Scheme 3)

Catalyst No.	Anchoring ligand	Rh content %	k^a $l\,mol_{Rh}^{-1}\,min^{-1}$
1	$(EtO)_3SiCH_2PPh_2$	0·5	35·9
2	$(EtO)_3Si(CH_2)_2PPh_2$	0·5	10·5
3	$(EtO)_3Si(CH_2)_3PPh_2$	0·5	13·0
4	$(EtO)_3Si(CH_2)_4PPh_2$	0·5	7·7
5	$(EtO)_3Si(CH_2)_5PPh_2$	0·5	4·3
6	$(EtO)_3Si(CH_2)_6PPh_2$	0·5	3·7
7	$(EtO)_2MeSiCH_2PPh_2$	0·35	34·6
8	$(EtO)Me_2SiCH_2PPh_2$	0·3	15·9
9	$(EtO)_2MeSi(CH_2)_2PPh_2$	0·5	13·6
10	$(EtO)_2MeSi(CH_2)_3PPh_2$	0·5	14·5

[a] Rh : P molar ratio = 1 : 2·5; reaction conditions: $p(H_2)$ = 114 kPa, 65°C, 14 mmol of 1-octene in 17·8 ml of toluene.

the phosphine is bonded to the surface only by means of one methylene group (catalysts *1* and *7*). On the other hand, least active were the catalysts bonded via the longest spacer in which rhodium atoms can relatively easily interact with each other. Comparison of the activity of the catalysts bonded via the same number of methylene groups but differing in the number of the ethoxy substituents at silicon (the pairs *1* and *7*, and *3* and *10*) shows that the catalytic activity is determined above all by the spacer length and not by the number of the ethoxy groups of the functionalization agent. This trend was not obeyed only by the catalyst *8* prepared by using (ethoxydimethylsilyl)methyldiphenylphosphine, which showed the lowest activity. In this case, however, the complex is bonded to the surface by only one siloxane bond and its mobility is thus increased (at least by rotation around the Si—O—Si bond). In connection with the results discussed above it is worth noting that while the activity of the catalyst bonded via propylene spacer is only little affected[40] by pore size, this factor plays a significant role in the case of the very efficient catalyst obtained with the use of (triethoxysilylmethyl)diphenylphosphine (the catalyst of type *1*, for designation see Table III). This conclusion is supported by the results presented in Table IV.

The difference in the catalyst activities demonstrated by data in Table III cannot be explained in terms of the induction effects of the substituents at phosphorus atom of the phosphines, as this difference has not been found in the case of homogeneous catalysts containing these functionalization agents[25]. Furthermore, there is also no correlation with the electron densities at phosphorus determined by ^{31}P NMR spectroscopy[28]. Similarly, also the hydrogenation of alkenes catalysed by rhodium(I) complexes with (trimethylsilylalkyl)diphenylphosphine ligands[43] is not affected by the induction effect of their ligands. The hydrogenation activities found[44] do not correlate with the electron density at phosphorus measured by IR spectroscopy[25] or by ^{31}P NMR spectroscopy[45].

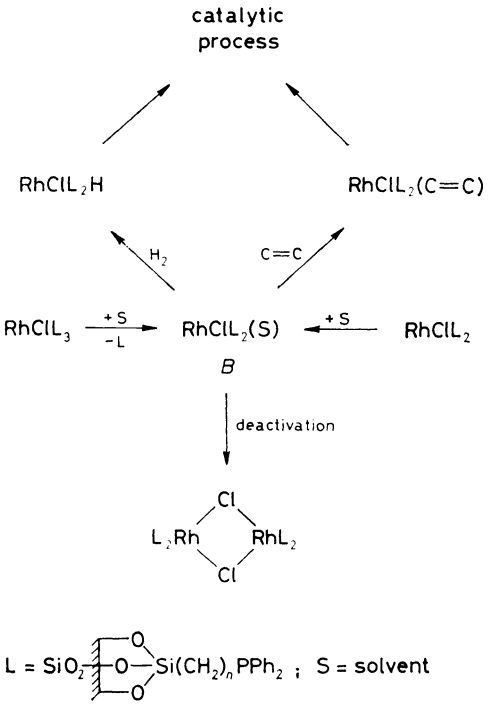
TABLE IV

Rate constants k (in l mol_{Rh}^{-1} min^{-1}) of hydrogenation of 1-octene catalysed by Rh(I) complexes immobilized by means of (triethoxysilylmethyl)diphenylphosphine

Mean pore diameter, nm	Rh content %	k^a
100	0·7	35·9
40	0·4	18·1
20	0·4	5·0

[a] For reaction conditions see Table III.

These facts agree well with the assumption that the surface-bonded rhodium(I) complex releases the phosphine ligand with formation of the free coordination site[41,42]. This is then occupied by the solvent or by some of the reactants. This species participates in the catalytic cycle either through the "hydride" or "unsaturated" route (Scheme 4). The complex of type *B* with the free coordination site is very



SCHEME 4

reactive and reacts not only with the solvent or reactant but also with another complex in its vicinity. Such an interaction results in formation of binuclear and even multinuclear agglomerates which are either inactive or less active than the complex *B* (Scheme 4). The undesired interactions just mentioned cannot be completely eliminated in the homogeneous phase. However, when the active complexes are anchored to support surface this interaction becomes less likely and its supression is the more effective the shorter and less mobile is the spacer. This comports with the high activity of the complexes anchored via the shortest and least mobile spacer[25] (i.e. methylene group).

The immobilization of homogeneous catalysts can exert favourable effect also on the selectivity of the reaction. This is demonstrated by the results obtained in the

hydrogenation of cinnamaldehyde[46], the products of which are cinnamic alcohol, hydrocinnamic alcohol and hydrocinnamaldehyde. Although the C=C group is much less reactive[47] than the C=C bond[48], the choice of reaction conditions shifts markedly product distribution[46]. Furthermore, heterogenization of $[RhCl(CO)_4]_2$ increases the yields of hydrocinnamic alcohol nearly ten times[46] (Table V).

By using $Rh(CO)_3(PPh_3)_3$ anchored to silica treated with (3-ethoxysilylpropyl)-diphenylphosphine we succeeded in favouring formation of cinnamic alcohol (at 70% conversion of the aldehyde the products contained 6% of hydrocinnamaldehyde, 22% of hydrocinnamic alcohol and 72% of cinnamic alcohol).

3.2. *Other Reactions*

One of the first reactions catalysed by the metal complexes bonded coordinately to inorganic supports was hydrosilylation[34] in which the immobilized catalyst could be recycled several times. Thus, for example, in hydrosilylation of 1-hexene by

TABLE V

Hydrogenation of cinnamaldehyde catalysed by homogeneous and heterogenized $[RhCl(CO)_4]_2$

Catalyst (0·12 mmol)	Cocatalyst mmol	Conversion %[a]	Selectivity, %[b]	
			A	B
SiO_2–$OSi(CH_2)_3N(Me_2)$. .$[RhCl(CO)_2]_2$	—	16	100	0
Homogeneous analogue	NEt_3 (1·8)	5	93	7
Amberlyst$(NMe)_2$. .$[RhCl(CO)_2]_2$	NEt_3 (7·2)	71	91	2[b]
Homogeneous analogue	NEt_3 (7·2)	10	96	4
SiO_2–$OSi(CH_2)_3PPh_2$. .$[RhCl(CO)_2]_2$	NEt_3 (7·2)	85	53	47
Homogeneous analogue	NEt_3 (7·2)	7	87	13
SiO_2–$OSi(CH_2)_3NMe_2$. .$[RhCl(CO)_2]_2$	KOH (0·08)	89	97	3
Homogeneous analogue	KOH (0·08)	7	87	13

[a] Conversion of cinnamaldehyde under the following reaction conditions: $p(H_2) = 4$ MPa, 107°C, 2·5 h, 8 mmol of cinnamaldehyde in 8 ml of toluene; [b] the products contained also 7% of cinnamic alcohol.

triethoxysilane catalysed by the Rh(I) complex anchored to silica by means of the $-SiCH_2CH_2PPh_2$ group, 77, 73, 71, and 34% yields of hexyltriethoxysilane were obtained in the first, second, third, and fourth use of the catalyst.

Complexes of this type were also used with success[49] in hydrosilylation of phenylacetylene by diethylmethylsilane. It is woth mentioning that in this, usually non-selective reaction, the addition to the first step was achieved with 91% yield. As another example, hydrosilylation crosslinking of polysiloxanes was catalysed efficiently by rhodium complexes on pyrogeneous silicon dioxide[50].

The above results made good starting point for a detailed study of the effect of the spacer structure on the activity of hydrosilylation catalysts[51] and also for verification of the conclusions arrived at in an analogous study of hydrogenation[25]. The catalysts prepared in the same way as for hydrogenation were tested in hydrosilylation of 1-hexene by dimethylphenylsilane[51] (Table VI).

The results show that the complexes bonded to the surface via two to six methylene groups exhibit nearly the same activity while the catalyst C-1 containing the shortest spacer is approximately ten times more active. This catalyst could be reused several times (at 15°C turnover numbers (s^{-1}) for the first, second, and third use were 4·3, 4·0, and 3·0, respectively). The same activation energy was found for the catalysts C-1 and C-4 (40·0 and 40·8 J mol^{-1}). It is markedly lower compared to the activation energy found for hydrosilylation of 1-hexene catalysed by other homogeneous or immobilized rhodium-phosphine catalysts[52] (60–92 J mol^{-1}). Within the range 0·07–0·25 mmol PPh_2/g and 0·02–0·74 mmol Rh/g, the activity was not affected by the degree of the coverage and the activity decrease manifested itself only for the support with the mean pore diameter of 2 nm.

TABLE VI

Catalytic activity of the complexes SiO_2–$OSi(CH_2)_nPPh_2$–Rh^I in hydrosilylation of 1-hexene by Me_2PhSiH (P : Rh mol. artio = 2·5 : 1, Rh conc. on support = 0·5%; 0·3 ml of benzene, 3 mmol of each reactant, Rh : Si mol ratio = $5 . 10^{-4}$: 1)

Catalyst	n	Turnover no. s^{-1}	E_A kJ mol^{-1}
C-1	1	19·72	44·0
C-2	2	2·32	
C-3	3	1·65	
C-4	4	1·82	44·8
C-5	5	2·02	
C-6	6	2·31	

The observed dependence of the catalytic activity on the length of the spacer can – similarly to hydrogenation – be explained by the absence of mutual interaction of the molecules bonded to the surface by the nonmobile, rigid spacer. This ensures that they act as mononuclear, while the complexes, the longer spacer of which makes them more mobile then form readily the less active dimers.

This idea is supported by ESCA spectra[51]. The bonding energies of the 3*d* level of rhodium are different for both types, the Rh $3d_{5/2}$ energy of the catalyst C-6 (309·1 eV) being very close to the value for binuclear rhodium(I) complexes[53] (309·0–309·4 eV). Also the high bonding energy of the 2*d* level of chlorine (199·5 eV) points to the bridge structure Rh—Cl—Rh. The $3d_{5/2}$ Rh bonding energy of the catalyst C-1 is lower then that of the precursor, $[RhCl(C_2H_4)_2]_2$, the analogue of which is supposed to be present on the surface. The far IR spectra[51] comport with the ESCA results, too. In the Rh-alkene region there are two absorption bands at 406 and 394 cm^{-1}. This fact can be explained by that the catalyst contains the two coordinated alkene ligands in the *cis*-position. The catalyst C-1 shows further the band at 296 cm^{-1} which is consistent with the end (Rh—Cl) arrangement. On the other hand, the bands at 274, 264, and 241 cm^{-1} showed by the catalyst C-6 can be ascribed to the bridge chlorine structure[54].

However, the catalysts bonded to the surface by means of the shortest spacer do not have to be necessarily always the most active ones. Thus, for example, the isomerisation of 1-pentene is catalysed best by the complexes bonded via the longest spacer[55]. This finding does not, however, contradicts the above discussed trends as in this case the catalytic intermediate proper is – similarly to the homogeneous catalysis – likely the dihydridorhodium(III) complex with no tendency to form multinuclear complexes. The situation is instructive by pointing to the importance of the knowledge of the course of homogeneous reactions when explaining the mechanism of the reactions taking place with immobilized catalysts.

4. CATALYST LEACHING AND ITS SUPRESSION

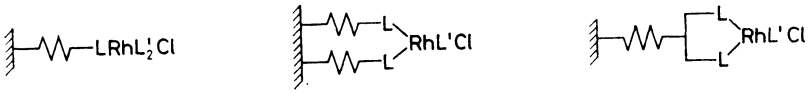
4.1. *Rhodium*(I) *Complexes*

One of the most important problems of immobilized catalysts is the question how to ensure their sufficient performance life and to supress the leaching of transition metal complexes to the liquid phase. In general, the solubilization of the anchored complex can proceed by the following ways:

– by the cleavage of the coordination bond between the ligand and the metal;
– by the cleavage of the anchored ligand from the support surface;
– by degradation of the support.

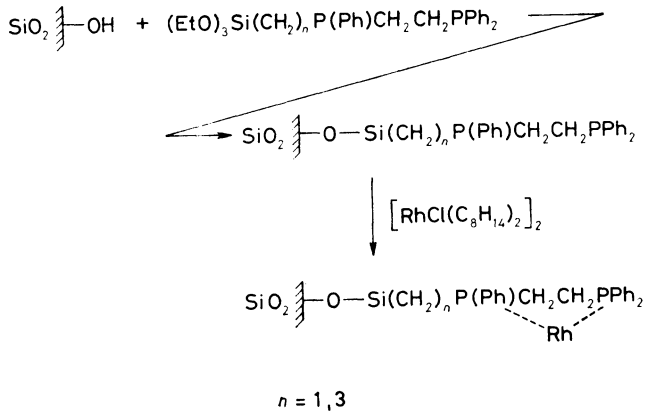
Of these processes, in the case of the inorganic supports functionalized by organosilicon compounds, the last two possibilities are very improbable. However, the

cleavage of the rhodium-phosphine coordination bond during hydrogenation was already proved experimentally[56]. This fact is not so surprising as the neutral rhodium(I) complexes are bonded to the surface by only one (structure *C*) or two anchoring ligands (structure *D*) and for formation of the free coordination site which is needed for the start of the catalytic cycle, at least one ligand has to be released[57]. If this is the anchoring ligand, the complex is solubilized, and that easier in the structure *C* then *D*, and likely with the great difficulty in the structure *E* (i.e. with the bidentate ligand).



C *D* *E*

For that reason we prepared a silyl-substituted bidentate phosphine to which the rhodium(I) complex was bonded as shown in Scheme 5.

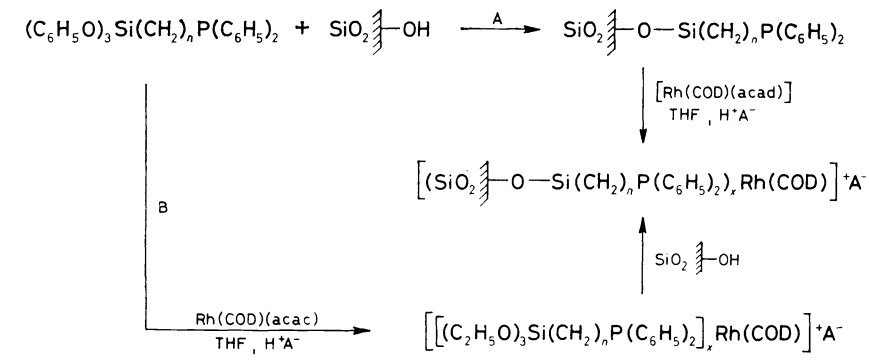


SCHEME 5

The activity and selectivity of both homogeneous and immobilized complex was similar, the metal was not solubilized, but as a consequence of the strong bond between the central metal and the bidentate ligand, the choice of the substrates to be hydrogenated was rather limited.

This led us to examine the cationic complexes of the type L_2RhRh (cyclooctadiene)$^+A^-$ where the free coordination site is not likely formed by the cleavage of the anchoring phosphine but by the release of the coordinated cyclooctadiene after its hydrogenation to cyclooctane. It should be mentioned, however, that the previous

experience with cationic rhodium(I) complexes was not too encouraging[58,59]. This could be due to the fact that the true analogue of the homogeneous complex has not been introduced on the surface. Therefore, we examined the two procedures[60,61] depicted in Scheme 6.



$n = 1,3$; HA = CH_3–C$_6$H$_4$–SO_3H ; acac = 2,4-pentadionate ; COD = 1,5-cyclooctadiene

SCHEME 6

The procedure A is frequently used in the synthesis of neutral rhodium(I) complexes and involves initial formation of the phosphinated support followed by the coordination of [Rh(COD)(acac)] in the presence of a strong acid. In the light of good results obtained in the preparation of Rh(I)-arenesulphonate complexes by other authors[62], *p*-toluenesulphonic acid was used also here in place of the usual strong inorganic acid. The reaction was instantaneous, the number of the coordinated phosphine ligands being determined above all by the steric reasons and surface density of the ligand at the coordination site and not by the total P : Rh mol. ratio. This seems to indicate that only small part of Rh atoms contains two coordinated phosphine anchoring ligands.

By contradistinction to it, the procedure B creates good conditions for formation of the surface complexes of uniform structure. It involves initial pre-formation of the soluble cationic rhodium(I) complex containing silyl-substituted phosphines, followed by anchoring of this complex to the support.

The so prepared immobilized cationic complexes catalysed hydrogenation of alkenes, alkynes and dienes. Although it was reported earlier[62] that the cationic Rh complexes containing monodentate phosphines are not catalytically active in hydrogenation of *Z*-α-acetamidocinnamic acid, the catalysts prepared with the use of alkoxysilyl-substituted phosphines were efficient catalysts of this reaction[60].

However, their activity depended markedly upon Rh : P mol. ratio (Table VII), the most active being the catalyst obtained at the ratio corresponding to the structure $[Rh(diene)L_2]^+$. The Rh : L ratio affects significantly also the stability of the catalyst, and at Rh : L = 1 : 1 the whole system is unusually sensitive to the traces of oxygen and decompose fast to the rhodium metal.

In the light of the dependence of the activity of homogeneous cationic rhodium complexes on the Rh : P mol. ratio one can interpret also the effectiveness of their heterogenized analogues. When the immobilized complexes were prepared by the procedure A which did not ensure the optimal Rh : P ratio (1 : 2) for all the active centres, the catalysts obtained were less active than homogeneous systems. Although they could be reused several times, their activity decreased fast on recycling due to decomposition to metallic rhodium, similarly as reported in other cases[58,59].

On the other hand when the synthesis was made by procedure B, ensuring thus the sufficient excess of the ligand for each immobilized molecule, the catalyst activity underwent dramatic changes. The immobilized complex was three to four times more active compared to the homogeneous analogue, in spite of the fact that the rate of the reactions catalysed by heterogeneous as well as heterogenized catalysts is slowed down by transport phenomena.

These data do not contradict with the results obtained in the hydrogenation of

TABLE VII

Hydrogenation of *Z*-α-acetamidocinnamic acid catalysed by homogeneous and heterogenized Rh complexes of the type $[RhL_x(COD)]^+$ p-$CH_3C_6H_4SO_3^-$

Rh : P mol. ratio	k (min^{-1}) for L[a]	
	$(EtO)_3SiCH_2PPh_2$	$(EtO)_3Si(CH_2)_3PPh_2$
	Homogeneous	
1 : 1	54	74
1 : 1·5	101	122
1 : 2	141	124
1 : 3	2	0
1 : 4	1	0
	Heterogenized	
Procedure A	82 (45[b]; 9[c])	13
Procedure B	424	544

[a] Ref.[60], reaction conditions: the Rh complex 0·028 mmol, $p(H_2)$ = 176 kPa, 40°C, 5 ml of ethanol and 5 ml of toluene; [b] 2nd use; [c] 3rd use.

alkenes catalysed by immobilized neutral rhodium(I) complexes[40] where it was found that the catalysts prepared by route B are less efficient than those obtained by route A. The reason is that both in solution and in the course of immobilization they can readily dimerize to the less active dimers. The cationic complexes do not have this property, and the prerequisite for their stability is the presence of two phosphines in the coordination sphere of the anchored complex. The fact that the cationic rhodium(I) complexes immobilized on inorganic supports having the proper stoichiometry of the surface complexes are stable and more active than their homogeneous analogues was used with advantage in development of the efficient immobilized enantioselective catalysts (Chapter 6).

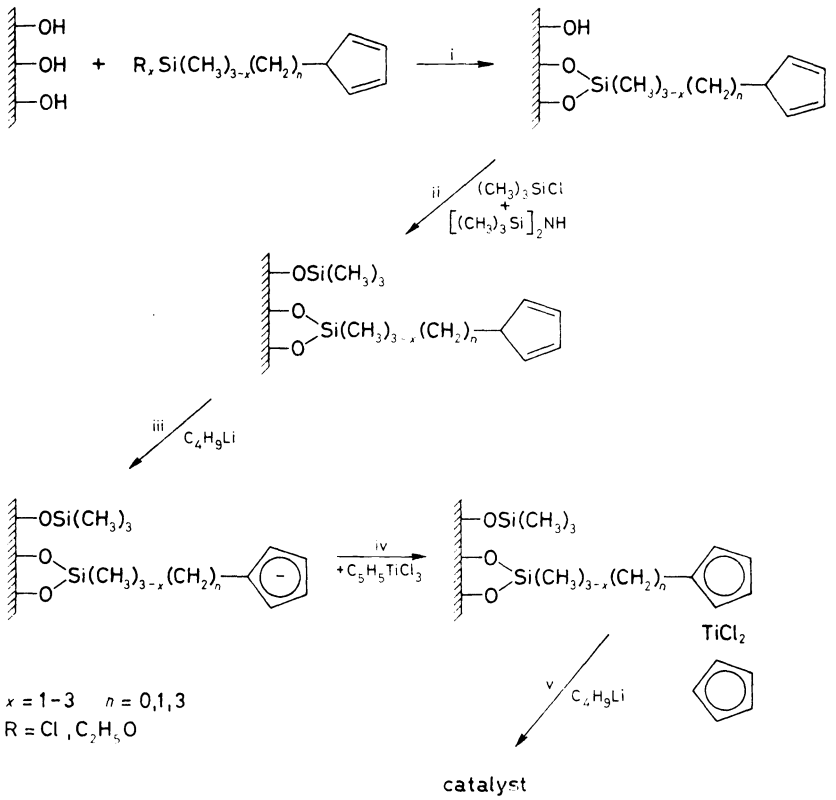
4.2. *Titanium Complexes*

Although the results discussed in the previous chapters were promissing, the catalysts were mostly based on the very expensive metal, rhodium. Therefore, we have paid attention to the synthesis of efficient hydrogenation catalysts based on the cheapter metals. One of them is the immobilization of titanium-cyclopentadiene complexes which exhibit[63] good hydrogenation activities in their reduced form. h^5-Cyclopentadienyl coordination bond is relatively strong, transition metal is thus well bonded and the danger of its ready dissociation is thus little. One can therefore expect that the eventual solubilization of the complex will be strongly supressed.

The previous works[64,65] indicated that the catalytic properties of immobilized complexes are influenced negatively by the free hydroxyl groups which are present on the support after its functionalization. To solve this problem we worked out the novel multistep synthesis of anchored titanium-cyclopentadiene complexes and were concerned with the more detailed examination of single steps, the extent of free hydroxyl groups blocking as well as with the structure of the immobilized complex.

The synthesis just mentioned is depicted in Scheme 7. The silica was functionalized by silyl-substituted cyclopentadienes[4,14] (i), the free hydroxyl groups were trimethylsilylated by the sterically less demanding silanes (ii), the cyclopentadienyl group was transformed into the cyclopentadiene anion (iii) to which the h^5-cyclopentadienyl-(trichloro)titanium(IV) complex was coordinated (iv), which then after reduction (v) afforded the hydrogenation catalyst proper[66].

When examining the number of free hydroxyl groups we have found after treatment of the support by triethoxysilylalkyl-substituted cyclopentadienes, that the OH group concentration decreased from the initial 2·25 mmol OH/g to 1·2 – 1·6 mmol OH/g, and by the additional trimethylsilylation with a trichlorosilane–hexamethyldisilazane mixture, to the value of 0·6 mmol OH/g, which could not be further changed[66]. However, it seems very likely that the residual OH groups are situated in so narrow pores that they will not interfere, which was then proved experimentally.



SCHEME 7

The other factor followed was the change of the accessibility of the pores after each step of the support treatment. As it is seen from Fig. 1, the treatment with (trialkoxysilylalkyl)cyclopentadiene and also an additional trimethylsilylation do not affect essentially the pore accessibility, only the final fixation of the bulky dicyclopentadienyltitanium(IV) complex decreases slightly the mean pore diameter (from 3·5 nm for the untreated silica to 2·8 nm for the supports with anchored Ti complex). This value is however still sufficient to ensure the access of the reactants to the active sites[66].

As the anchored bis(cyclopentadienyl)titanim(IV) complex was prepared by multistep synthesis, it was of interest whether its structure on the support corresponds to the crystalline bis(cyclopentadiene)dichlorotitanium(IV) complex. Table VIII presents bonding Ti $2p_{3/2}$ data obtained by ESCA for both the homogeneous and heterogenized complexes[66].

It becomes evident that the bonding energies for all the Ti complexes studied differ only within experimental errors (E_B = 457·5 eV) and correspond to the oxidation

state between +2 and +3. This formal oxidation state comports with the idea that the electrons are withdrawn from titanium mostly by the chloride anions, while – similarly to ferrocene – there exists a significant back donation from the cyclopentadienyl anion to the central metal atom.

As the other bonding energies of the anchored complexes differ only slightly from the values for the crystalline $(C_5H_4)_2TiCl_2$ one can assume that both types of Ti complexes are of very similar structure, the free hydroxyl groups do not enter the coordination sphere of the titanium and thus do not affect its catalytic activity.

To get the active catalyst, the immobilized titanium complex was reduced with butyllithium (step v in Scheme 7). The presence of the low valent titanium complexes after reduction of the anchored analogue was proved by ESR spectroscopy[67], which further confirmed that also after reduction the reduced titanium complexes remain firmly bonded to the support. The anisotropic ESR spectra which could be ascribed to the stabilized Ti(II) complexes, can be divided into two regions, one

TABLE VIII
Bonding energies of the titanium complex (accuracy ±0·2 eV)

Complex	Energy, eV[a]			
	Cl(2*p*)	C(1*s*)	Si(2*p*)[b]	O(1s)
$(C_5H_5)_2TiCl_2$	198·8	285·0	—	532·7
SiO_2–$OSi(CH_2)_3C_5H_4TiCl_2(C_5H_5)$	199·1	284·8	103·4	532·8
SiO_2–$OSiCH_2C_5H_4TiCl_2(C_5H_5)$	199·1	284·7	103·4	532·6

[a] Taken from ref.[66]; [b] used as the internal standard.

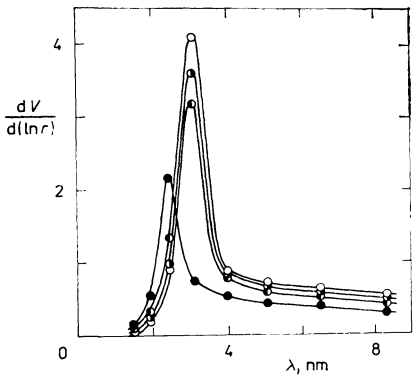
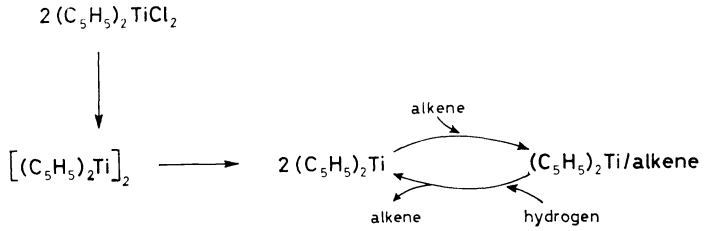


FIG. 1
Changes of pore size distribution during immobilization of Ti-cyclopentadiene complexes. ○ Starting silica, ◑ silica after treatment with the silyl-substituted cyclopentadiene (step i in Scheme 7), ◐ after trimethylsilylation (ii), ● after coordination of the Ti complex (iv), ref.[66]

with $g_{\perp}$ 1·999 up to 2·007 and the other with $g_{\parallel}$ 1·933 up to 1·945. Such complexes are not present in the homogeneous phase. The activity of the reduced immobilized Ti complexes was then examined in a kinetic study[67].

With the aim of better understanding of the mechanism of the action of the above catalysts, the behaviour of the homogeneous analogues was studied first in more detail. It was found that the reduced titanocene complexes catalyze hydrogenation of 1-alkene under normal pressure and at the temperatures 40–60°C. The reaction is zero order in hydrogen, the first order in the alkene and, unexpectedly, the half order in the catalyst. The activation energy of the reaction is small and the activation entropy is negative ($\Delta H = 24\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S = -128\ \mathrm{J\ mol^{-1}\ K^{-1}}$). These results were not compatible with the hydrogenation mechanisms proposed so far in the literature. This led us to propose the scheme depicted bellow (Scheme 8).



SCHEME 8

In this scheme the starting titanium(IV) complex is reduced to the dimeric low-valent titanium complex which is the most probable source of the highly active monomeric intermediates. The latter coordinates alkene in the rate determining step (as the rate of the hydrogenation depends on the alkene structure). As the isomerization of alkenes was not observed, the coordination of alkene is most likely followed by the fast attack of hydrogen, leading to the cleavage off of the alkane, the regeneration of the monomeric catalytic intermediate and the completion of the catalytic cycle. This proposal is supported also by the dependence of the reaction rate on hydrogen concentration[67].

On using the heterogenized Ti complexes in hydrogenation of 1-octene, nearly the same activation parameters and the same reaction orders in hydrogen and alkene were observed. The reaction rate did not depend on the catalyst concentration but on its amount (the result usual in the heterogeneous catalysis). This indicates that during hydrogenation reaction the anchored complexes remains bonded firmly to the support.

Data presented in Table IX show that there exists the distinct dependence of the activity of the reduced titanium catalysts on the length of the spacer between the support and cyclopentadienyl group. It is evident that the complex immobilized

by means of the shortest spacer ($n = 0$) is the most efficient catalyst. This is in harmony with the above proposed reaction mechanism. It becomes obvious that the shorter and less mobile spacer supresses mutual interaction of two "naked" catalytic intermediates, the dimerization of which is likely the reason for the activity decrease observed. The opposite situation arises in the case of the longer and more mobile spacers ($n = 1$ or 3) and with the homogeneous catalyst, resulting in the fast loss of catalytic activity during the hydrogenation.

The reduced anchored titanium complexes can be separated from the reaction mixture and reused several times after washing. Although the reuse of the catalyst was accompanied by a certain decrease in the catalyst activity (Table X), caused

TABLE IX

Hydrogenation of 1-octene catalysed by the reduced anchored titanium complexes of the type SiO_2–SiO_2–$OSi(CH_2)_n$-C_5H_4-$TiCl_2(C_5H_5)$ ($n = 0, 1, 3$)

Spacer n	k^a / l mol^{-1} s^{-1}	Reaction order in	
		alkene	hydrogen
3	0·75	1·07	0
1	2·93	1·00	0
0	3·26	0·98	0

[a] Taken from ref.[67]; reaction conditions: catalyst amount = 0·06 mmol Ti, $c_{alkene} = 0{\cdot}291$ mol . . l^{-1}, $p(H_2) = 96{\cdot}16$ kPa, 60°C, Ti : Li mol. ratio = 1 : 10, total volume 12 ml (toluene as the solvent). The rate constant k is linearly dependent on the catalyst amount.

TABLE X

Dependence of the initial rate r^0 and conversion of the alkene on the reuse of the anchored Ti-cyclopentadiene catalyst in the hydrogenation of 1-octene

Use[a]	r^0, mol s^{-1}	1-Octene conversion, %[b]
1st	5·2	78
2nd	5·0	75
3rd	5·0	69
4th	3·4	53

[a] Ref.[67], for reaction conditions see Table IX, the Ti catalyst with the spacer $n = 3$; [b] after 15 min.

likely by contamination of the catalyst during separation and washing, this drawback can be overcome by a continuous process.

The titanium catalysts described in this section are true heterogenized catalysts which remain bonded to the surface during the reaction and their reuse. Furthermore, their hydrogenation activity (calculated per transition metal atom) achieves that of the expensive rhodium complexes.

5. CATALYSTS IMMOBILIZED VIA ADSORBED LIGAND

In addition to the ways described in preceding chapters, in which immobilization was realized with the use of the support functionalized by the anchoring ligand bonded chemically to the support surface, also immobilization to the soluble polymers has been sometimes investigated. The advantage of this procedure is that transition metal complexes act here under conditions which are close to the homogeneous catalysis. Its disadvantage lies in the difficult separation of the catalyst from the products. A certain compromise is the situation where a polymer containing an anchoring ligand is adsorbed on the support. In many cases the interaction of the polymer with the support is so strong that such an immobilization becomes essentially irreversible. In a systematic study of the catalysts anchored to inorganic supports we paid attention also to this immobilization.

Already in the year 1972, hydrosilylation of alkenes was effected with the rhodium catalyst immobilized on the support impregnated by polysiloxane containing cyano groups[68]. This led us to study the synthesis of other suitable polymers. Hydrogen-(methyl)dimethylsiloxane copolymer modified with octadecene[69] found use in chromatography[70] and that modified with allyl cyanide[71] became the easily available polymer ligand for immobilization of platinum hydrosilylation catalysts[72]. In order to prevent metal leaching from the nonporous support, we worked out the synthesis of poly(methylmethacrylate) bonded to the surface of the microparticular silica[73] functionalized by (3-methacryloxypropyl)trimethoxysilane.

Nevertheless, the more important compounds for immobilization are the liquid polymers containing phosphine groups capable of coordination with transition metals. One of the promissing routes proved to be the synthesis of poly(butadienyl)-phosphines[74] which started from the reaction of "living" polymers of the anionic polymerisation of butadiene with chlorophosphines (Eqs (*14*) and (*15*)). The chiral chlorophosphine was used to prepare the optically active polymeric phosphines[74].

$$C_4H_9Li \xrightarrow{C_4H_6} C_4H_9(C_4H_6)_nLi \xrightarrow{ClPR^1R^2} C_4H_9(C_4H_6)_2PR^1R^2 \qquad (14)$$

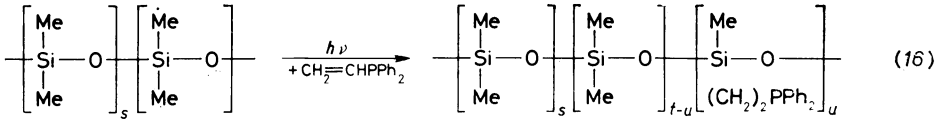
$$LiC_4H_6Li \xrightarrow{C_4H_6} Li(C_4H_6)_nLi \xrightarrow{ClPR^1R^2} R^1R^2P(C_4H_6)_nPR^1R^2 \qquad (15)$$

$$R^1,R^2 = \text{phenyl, menthyl}, \; n = 5-500$$

Poly(butadienyl)diphenylphosphine was then used[75] in the gas phase hydroformylation of propene catalysed by the so called SLP (supported liquid phase) catalysts. Unfortunately, likely due to crosslinking of the polymer, the catalyst lost fast its activity.

If the reactants and products are gaseous and thus the metal leaching cannot occur, also molten phosphines can be used[75] for immobilization. In such an arrangement the same activity and selectivity as in the homogeneous phase has been achieved[76], being better than in the hydroformylation catalysed by Rh(I) complexes containing secondary phosphines as ligands[77].

With the aim to understand better the action of the catalysts bonded to linear polymers, we prepared polysiloxanes substituted at silicon by the ω-(diphenylphosphino)alkyl group[78]. These polymers were obtained by polycondensation of (3-diphenylphosphinopropyl)methyldiethoxysilane, eventually by the addition of vinyldiphenylphosphine to poly[(dimethyl)(methylhydrogeno)]siloxane (Eq. (*16*)).



(16)

$s : t = 5 \cdot 5 : 1$

$s : (s + t - u) = 1 : 40$

Of these polymers, rhodium(I) complexes were prepared by treatment with $[RhCl.(cyclooctene)_2]_2$ and their activity was studied kinetically in the hydrogenation of 1-heptene at atmospheric pressure. It was found, that similarly to other homogeneously catalysed reactions[40,79], the hydrogenation is the first order in the catalyst. The reaction order is not affected by the number of methylene groups between phosphorus and silicon or by the density of the phosphine groups on the polymer chain, and in the region studied it was also independent of the Rh : P mol. ratio The activity of rhodium(I) complexes coordinated to the polymers with high density of phosphine groups was practically the same as the activity of the catalysts with monomer ligands. The ligand in excess showed similar effect. However, the stability of the polymer catalysts was markedly greater.

Another situation has been encountered in the case of the polymers with the low density of anchoring ligands where the coordination of two phosphine groups to one rhodium atom is less probable. In that case the catalyst activity was markedly less supressed by excess ligand and the catalytic solutions prepared in situ showed unchanged activity even after ten days[78].

Information about the effect of the mobility of polysiloxane chain on the catalytic activity was obtained by depositing the catalysts in low concentrations on the inorganic support and determining their hydrogenation activities (Table XI) in dependence on the way of their preparation.

The solution of the complex prepared by coordination of Rh(I) to phosphinated polysiloxane (see Eq. (*16*)) was adsorbed as such on the inorganic support. The catalyst so prepared showed lower activity than homogeneous one, but it could be reused and was also sufficiently stable[78]. The most efficient catalyst was however that prepared by the coordination of Rh(I) to the support impregnated by the polymer ligand.

This result agrees well with the previous findings concerning the hydrogenation[5,40] and hydrosilylation[51] catalysed by the complexes immobilized on supports with the use of functionalized monomer silyl-substituted phosphines (see Chapters 2.1. and 2.2.). It further supports the assumption that the immobilized catalysts are more active when the heterogenization makes dimerization of the catalytically active intermediates impossible.

6. ENANTIOSELECTIVE CATALYSTS

One of the most attractive fields of homogeneous catalysis is the catalysis by chiral transition metal complexes, as the tool for preparing very valuable optically active products from prochiral reactants. As most of the selective catalysts are based on rhodium complexes, their heterogenization has attracted increasing interest[80,81], the special attention being paid to the catalysts for hydrogenation of dehydro-α--amino acids (e.g. phenylalanine) or synthesis of drugs (DOPA).

In the course of our studies we prepared the supports with chiral centres derived

TABLE XI

Rate constants k ($l\ mol^{-1}\ min^{-1}$) of hydrogenation of 1-heptene catalysed by Rh(I) complexes bonded to the phosphinated polysiloxane (Eq. (*16*)) (1 ml of 1-heptene, 9 ml of toluene, $p(H_2) =$ = 115 kPa, 64°C)

Catalyst	k
In solution	10
Prepared in solution, then transferred on polymer	4·6; 4·7[a]; 4·4[b]
Support impregnated by the ligand, then Rh(I) coordinated	15·8

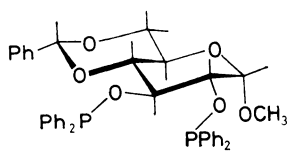
[a] Reaction components distilled off and the catalyst reused; [b] after aging of the catalyst for 10 days

from phenylethylamine[33], D-arabitol[22] and menthyl group[24,26,74]. The synthesis of (3-triethoxysilylpropyl)phenylmenthylphosphine[24] as one of the first chiral functionalization agents allowed us to study solubilization of the anchored complex[56] based on the fact that enantioselectivity reflects sensitively changes in the neighbourhood of the reaction centre.

By the methods described in Chapter 3.1. rhodium(I) complexes were immobilized on silica and porous glass. The activity of these complexes was tested by hydrosilylation of acetophenone and ethyl phenyl ketone by diphenylsilane[56] (Eq. (*17*)). The reaction proceeds well and affords a mixture of the alkoxysilane and the starting ketone. The optical yields were however small, only in the homogeneous phase, with the use of the excess (3-triethoxysilylpropyl)phenylmenthylphosphine and at low temperatures the yields were comparable to those obtained with DIOP as the ligand[80]. The study also demonstrated that the surface-bonded complex undergoes solubilization by the cleavage of the anchoring ligand due to coordination of some of the reactants. This fact was taken into account during development of other enantioselective catalysts.

$$\text{>CH—C(/)=O} + R_2SiH_2 \begin{cases} \nearrow \text{CH—CHOSiR}_2\text{H} \xrightarrow[H_2O]{CH_3OH} \text{>CH—CHOH} \\ \searrow \text{C=C—OSiR}_2\text{H} \xrightarrow[H_2O]{CH_3OH} \text{>CH—C=O} \end{cases} \qquad (17)$$

One of them was a rhodium(I) complex containing novel bidentate chiral ligand – methyl 4,6-O-benzylidene-2,3-O-(diphenylphosphino)-β-D-glucopyranoside (Glup)

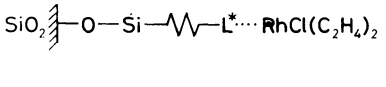


Glup

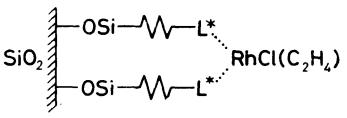
which in addition to hydrogenation[82] shows also high enantioselectivity in hydrosilylation of ketones by diphenylsilane[83], as demonstrated in Table XII. The great advantage of this system is that by contradistinction to the other chiral ligands[84], the silyl enol formation is supressed, and the optical yields ranked at that time among the highest. The system Rh–Glup after immobilization on silica by impregantion showed same enantioselectivity as the homogeneous analogue (e.e. 39%), but its enantioselectivity decreased on reuse (e.e. 14%). This decrease was accompanied by the increased formation of the silyl enol ether, which indicates that the catalytically active species does not contain the donor ligand.

The series of ω-(triethoxysilylalkyl)dimenthylphosphines of the type $(EtO)_3Si.(CH_2)_nPMen_2$ (n = 1, 3, 5) made it possible to study the factors determining the behaviour of immobilized chiral catalysts in more detail. It is however worthy of note that these phosphines exhibit higher basicity than triphenylphosphines studied earlier, being comparable to tricyclohexylphosphines, As a consequence, their rhodium(I) complexes are less prone to form dimers or multinuclear agglomerates compared to rhodiumtriphenylphosphine complexes[85].

A kinetic study of the rhodium(I) complexes containing the above alkoxysilyl--substituted alkyldimethylphosphines showed that at least two phosphines should be coordinated to the rhodium atom to ensure high optical yields[26]. It was therefore assumed that the surface complex *G* would exhibit higher enantioselectivity than the complex *F*.



F



G

This led us to choose such an immobilization procedure which would ensure formation of the former complex. The activity of the Rh complex so obtained (pentylene as the spacer (n = 5), P : Rh mol. ratio = 6 : 1) is illustrated in Table XIII. The optical yields obtained in the hydrogenation of itaconic acid were the best

TABLE XII

Hydrosilylation of acetophenone and phenyl ethyl ketone by diphenylsilane catalysed by the system Rh–Glup

Reaction temp., °C[a]	(*S*)-$C_6H_5CH(OH)CH_3$			(*S*)-$C_6H_5CH(OH)C_2H_5$		
	react. time, h	yield %	e.e.[b] %	react. time, h	yield %	e.e.[b] %
0	20	98	47	40	96	34
25	4	97	38	10	97	24
50	2	96	27	2	94	20

[a] Data taken from ref.[83], reaction conditions: 12 mmol of Ph_2SiH_2, 10 mmol of ketone, 40 mmol of Rh(I), Rh : P mol. ratio = 1 : 2, 15 ml of toluene; [b] e.e. enantiomeric excess.

reported so far for this reaction. On the other hand, the catalysts with methylene group ($n = 1$) as the spacer or with P : Rh mol. ratio = 3 to 4 : 1 were inferior both in the optical yields achieved and in their effectiveness. Although the activity and enantioselectivity of the rhodium(I) dimenthylalkylphosphine complexes was high, they suffered from metal leaching on repeated use.

As already mentioned, the greater resistance to metal leaching can be expected for the complexes containing bidentate phosphine ligands[29], while the cationic Rh(I) complexes are by far more stabilized against dimerisation of active centres[60]. These two aspects are combined in the cationic rhodium(I) chelates containing phenyl 4,6-O-(*R*)-benzylidene-2,3-O-bis(diphenylphosphino)-β-D-glucopyranoside (Ph-β-glup) bonded to the commercial sulphonated styrene-divinylbenzene ion exchangers[86]. These anchored catalysts were of great interest as they showed the increased enantioselectivity compared to the homogeneous analogues. Nevertheless, their disadvantage was in that the sulphonic acid groups of the organic supports used were located within polymer mass and thus their interaction with the rhodium(I) complex was more difficult. Furthermore, because of the texture of the supports, the immobilized catalysts were little active in the reactions of substances having molecular mass above 200.

These facts initiated our study of inorganic supports. We expected that they would ensure better mechanic properties, resistance to solvents, choice of the suitable texture, and especially the location of sulphonic acid groups on the surface. Commercial silica was functionalized[19] by (3-phenoxy)propyltrichlorosilane[18], then sulphonated under mild conditions[88] and the support was used to immobilize $[Rh(Ph\text{-}\beta\text{-}glup)(cyclooctadiene)]^+BF_4^-$ complex (Scheme 9). The behaviour of this catalyst in comparison with the homogeneous analogue and the complex bonded to an organic support is shown in Table XIV. The results demonstrate that the

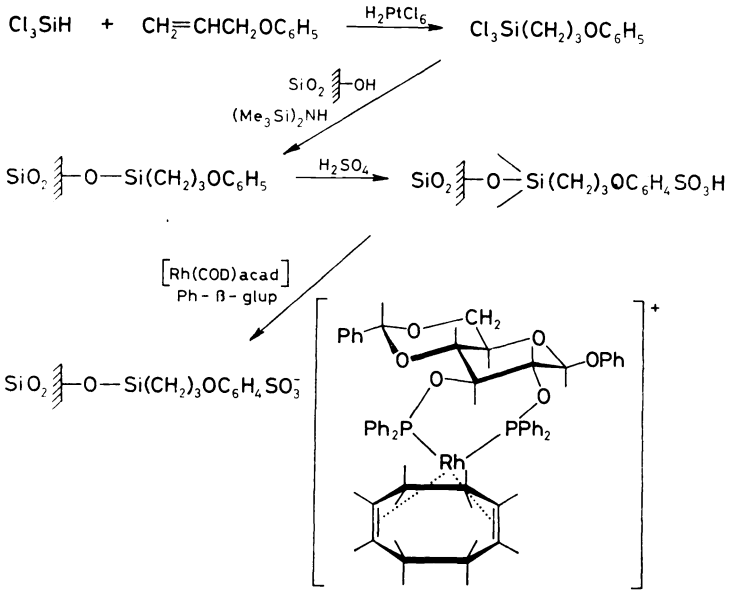
TABLE XIII

Catalytic activity and enantioselectivity of the complex $SiO_2\text{–}OSi(CH_2)_5PMen_2Rh^I$

Substrate[a]	Reaction time, h	Conversion %	e.e.[b] %
1-Acetamidocinnamic acid	3	100	87 (*R*)
1-Acetamidoacrylic acid	7	100	18 (*S*)
Itaconic acid	20	67	83 (*S*)
Methyl 1-acetamidocinnamate	78	70	9 (*R*)

[a] Ref.[26], reaction conditions: substrate 1 mmol, Rh(I) 0·01 mmol, Rh : P mol. ratio = 1 : 2, $p(H_2)$ = 0·1 MPa, 25°C, 15 ml of methanol; [b] enantiomeric excess.

complexes bonded to inorganic supports exhibit the same enantioselectivity as the catalysts immobilized on organic supports but their activity is significantly in-



SCHEME 9

TABLE XIV

Hydrogenation of methyl (*Z*)-α-acetamidocinnamate catalysed by Rh(Ph-β-glup) chelates immobilized on inorganic and organic supports and by the homogeneous Rh(I) complex ($t_{1/2}$ half-life in min^{-1}, e.e. enantiomeric excess in %)

Use[a] no.	Inorganic support[b]		Organic support[c]		Homogeneous catalyst[d]	
	$t_{1/2}$	e.e.	$t_{1/2}$	e.e.	$t_{1/2}$	e.e.
1	27·5		133		6	91·8
2	28		114			
3	34·5	94·8[e]	155	94·2[e]		
4	39·5		197			
5	45		—			

[a] Reaction conditions as in Table XIV, the catalyst was separated by filtration, washed and reused; [b] ref.[38]; [c] ref.[86]; [d] ref.[87]; [e] the average value of several measurements.

creased. This finding can be ascribed both to the more suitable texture of the support and to the location of sulphonic acid groups on support surface. The still better results were achieved in the hydrogenation of the less bulky methyl 2-N--acetamidoacrylic acid where the Rh(Ph-β-glup) complex on silica was reused twenty times with no change of enantioselectivity (e.e. = 94·1 ± 0·2%) and only with small decrease of its activity (the half-life increased from initial 2·2 min^{-1} to 3·5 min^{-1} after 20 uses). In the hydrogenation catalysed[86] by the homogeneous complex the half-life was 2 min and in the case of the organic polymer 15 min. It is worthy of mentioning that the so high enantioselectivity has been obtained so far only in the pressure hydrogenation[89].

Summarizing, these results are promissing with respect to the perspective industrial application of these catalysts in producing expensive chemical specialities and pharmaceutical products. The stable, rigid chelates bonded via ionic bond to the support seem to be at present the best type of the anchored enantioselective catalysts. The coordination sphere of transition metal acts here as in the homogeneous catalysis. At the same time, the catalysts are bound by ionic forces to the support so that in the reactions in nonaqueous solvents there is essentially a minimal danger of catalyst leaching.

7. IMMOBILIZED BIOCATALYSTS

In the preceding chapters we were concerned mainly with the catalytic centres which would ensure the high activity and selectivity of heterogenized complexes. In the case of immobilized enzymes the situation is quite different. During millions years of its existence the Nature created the very active selective catalysts acting in aqueous media under mild conditions very specifically, making use of the synergic effect based on the "lock and key" concept.

That is why one cannot expect that immobilization of the enzyme will result in the increase of its activity but on the contrary one has to seek for such immobilization methods which would not affect much this property. The reason for the immobilization of enzymes lies in that they can be obtained more stable, easily separable and with long performance life. The greatest danger in the application of immobilized enzymes is in their cleavage from the support and their deactivation either by blocking active centres by chemical reaction or by their hindered accesibility for the reactants. The above reasons led us to center our attention to the choice of suitable supports.

In contradistinction to the heterogenization of transition metal complexes, it is not usually necessary here to synthesize novel functionalization alkoxysilyl-substituted ligands, as the enzymes are immobilized frequently with the use of the amine, thiol, or oxiranes groups present in commercially available agents[12]. One of the great advantage of inorganic supports for the immobilisation of biocatalysts is

their nearly infinite resistance to microbial attack. The applicability of these supports for enzyme immoblization was verified[90] by comparison of the epoxypropyl-substituted silica with "traditional" organic supports, which confirmed some advantages of the inorganic supports. When comparing[91] the suitability of the silica modified with epoxypropyl groups with the poly(acrylate) support Supergit C containing oxirane groups in the immobilization of endopolygalacturonase we have found that the inorganic supports was capable of anchoring the greater amount of the enzyme. The samples could be stored for several months without loss of their activity, and in the cleavage of sodium pectate their behaviour corresponded to the Michaelis–Menten kinetics.

In the enzyme immobilization some problems represent nonspecific sorptions and transport phenomena connected with the location of bulky enzyme molecules in pores, as it is necessary to ensure also after enzyme immobilization the access of their active sites for the usually macromolecular substrate. It is evident that for that reason the suitable support for immobilization will be that with prevailing external surface. The study of the model reaction of the macromolecular chain[73] showed that the reaction centre bonded to a nonporous support exhibits identical activity and selectivity as the same centre in solution. Therefore, the immobilization of enzymes has been carried out with a pyrogeneous, highly dispersed silicon dioxide[92]. After introduction of the surface-bonded aminopropyl groups followed by treatment with glutaraldehyde, the following enzymes were successfully imobilized: chymotrypsin, trypsin, pancreatic trypsin inhibitor, and serumalbuminii ovalgumin. In this case it was possible to fix such an amount of the enzyme (e.g. 59 mg of chymotrypsin per g of the support) that was otherwise achieved only with porous supports. The portion of the enzyme bound by nonspecific sorptions and by affinity was 1 : 30, and its activity (determined both by the low molecular Suc-L-Phe-pNS and by the high molecular hemoglobin) was 40–60% of the native enzyme turned out to be suitable for the batch arrangement of the reaction with the enzyme separation by centrifugation.

Comparison of the effects of nonporous and porous supports on the endopolygalacturonase immobilized[93] via amine, carboxyl, and oxirane groups demonstrated that the nonporous support affects the selectivity of the immobilized enzyme by far less than the other supports. The reason is the absence of additional effects caused by the size of reactants (exclusion effect, size, etc.).

With the aim to study the effect of the support on the amount and activity of immobilized enzymes we have immobilized pepsin on porous glass, nonporous glass and ground quartz[94]. Pepsin was chosen as one of the readily available and relatively cheap enzymes which participate in the selective cleavage of some macromolecular substrates such as antibodies or proteins in food.

With regard to the fact that pepsin as the protein containing a great amount of aspargyl units is immobilized likely via the carboxyl units, the supports were treated

with (3-aminopropyl)triethoxysilane and then pepsin was fixed by the carbodiimide method. It was found that the amount of the immobilized enzyme corresponds roughly to the amount of the aminopropyl groups on the support[94].

All the products so obtained were highly stable and could be stored at 8°C for at least one month. The greatest amount of the enzyme, as well as the highest proteolytic activity was exhibited by the catalyst derived from nonporous silica[94]. Similarly, also the degree of the preserved activity of the native enzyme was very high (64%), its decrease being very likely caused by formation of agglomerates of single particles, as detected by the laser beam scattering. The activity decrease found for the quartz-based catalyst (26%) is not due to the above mentioned agglomeration (as the catalyst is dispersed into individual particles) but probably by the too high concentration of the amino groups (65 μmol/m^2) which attract electrostatically pepsin, supressing thus its proteolytic activity. On the other hand, the unchanged activity of the enzyme immobilized on wide pore glass is extraordinary and speaks for the essentially unlimited penetration of the substrate to the enzyme. These supports are however very expensive.

In connection with these studies it was of interest to examine the effect of the texture of the easier available silica on the catalytic behaviour of the immobilized endopolygalacturonase[95]. As the pore size affects not only the amount and activity of the immobilized enzyme but also its selectivity, the enzyme was bonded to the supports of varying pore size and the cleavage was followed both for the low molecular and high molecular substrates. The silica treated with [(3-2',3'-epoxypropoxy)-propyl]trimethoxysilane was used to immobilize directly the enzyme. The results showed that the support texture plays an important role, affecting access to the bonded enzyme and that in the 20 nm pores and smaller, the activity of the endopolygalacturonase is practically lost. The enzyme immobilized on the supports with the mean pore diameter 50 to 100 nm operates such that the high molecular chain of sodium pectate is cleaved preferentially at the ends of the chain, and only on the supports with pores still larger (Fractosil 2500) it reacts analogously to the free enzyme, i.e. the cleavage of the substrate takes place in the middle of the chain. Similar results were obtained also in the cleavage of the ^{3}H-labbeled tetra(D-galactosiduronic) acid.

For some applications, however, the column arrangement seems to be favoured over batch processes. In these cases, the fine particle supports are not suitable. Contrarily, in the enzymatic treatment of some natural substances (the clarification of juices or the removal of the substances causing turbidity of bear or wine) hydrodynamic properties of the supports are their primary and desicive characteristics.

In the light of the above facts, endopolygalacturonase was immobilized on ceramic rings (4 × 4 mm with the 2 mm hole). The support was treated first with hydrochloric acid, then with (2-aminopropyl)triethoxysilane, and finally with glutaraldehyde. Then, endopolygalacturonase was anchored to this support (content of

–CHO groups 1·48 μmol g^{-1}). The immobilized enzyme (63 μm per 1 g support) preserved 44% of the activity of the native enzyme. This biocatalyst could be stored at 25°C for 8 months without loss of its activity. Its performance stability was also very high; after continuous performance for 3 months in the cleavage of sodium pectate, its activity decreased by only 30 per cent. These properties, along with good hydrodynamic behaviour makes industrial application of this catalyst very promissing.

REFERENCES

1. Čapka M., Svoboda P., Černý M., Hetflejš J.: Tetrahedron Lett. *50*, 4787 (1971).
2. Čapka M., Svoboda P., Kraus M., Hetflejš J.: Chem. Ind. *1972*, 650.
3. Svoboda P., Čapka M., Hetflejš J., Chvalovský V., Jahr H., Pracejus H.: Z. Chem. *12*, 153 (1972).
4. Pitman C. U. in: *Comprehensive Organometallic Chemistry* (G. Wilkinson, F. G. A. Stone and E. V. Abel, Eds), Vol. 8, p. 353. Pergamon Press, Oxford 1982.
5. Yermakov Y. I., Kuznetsov B. N., Zakharov V. A. (Eds): *Catalysis by Supported Complexes.* Elsevier, Amsterdam 1981.
6. Michalska Z. M., Webster D. E.: Chem. Technol. *1975*, 117.
7. Messing R. A.: *Immobilized Enzymes for Industrial Reactors.* Academic Press, New York 1975.
8. Švec F.: *Polymerní katalyzátory.* Academia, Praha 1987.
9. Parshall G. W.: *Homogeneous Catalysis*, p. 227. Wiley, New York 1980.
10. Pracejus H.: *Koordinations chemische Katalyse organischer Reaktionen*, p. 233. T. Steinkopf Verlag, Dresden 1977.
11. Hartley F. R., Vezey P. N.: Adv. Organomet. Chem. *15*, 189 (1977).
12. Hetflejš J.: Chem. Listy *77*, 843 (1983).
13. Čapka M., Rmoutil M., Rosenberg I., Holý A.: Czech. 215 743.
14. Vondráček P., Čapka M., Schaetz M.: J. Appl. Polym. Sci. *24*, 1619 (1979).
15. Čapka M., Rmoutil M., Hetflejš J.: Czech. 213 696.
16. Voronkov M. G., Lukevits E. J.: *Gidrosilirovanie, gidrogermylovanie, gidrostanilirovanie.* Izd. Akad. Nauk Latviis SSR, Riga 1964.
17. Marciniec B.: *Hydrosilowanie.* Paňnstwowe Wydawnictvo Naukowe, Poznaň 1989.
18. Čapka M., Rosenberg I., Holý A., Hetflejš J.: Czech. 224 790.
19. Čapka M., Rosenberg I., Vozka S.: Czech. 236 317.
20. Kopylova L. I., Sigalov M. V., Satsuk E. N., Čapka M., Chvalovský V., Pukhnarevich V. B., Lukevit E., Voronkov M. G.: Zh. Obshch. Khim. *51*, 385 (1981).
21. Pukhnarevich V. B., Kopylova L. I., Čapka M., Hetflejš J., Satsuk E. N., Sigalov M. V., Chvalovský V., Voronkov M. G.: Zh. Obshch. Khim. *50*, 1554 (1980).
22. Čapka M., Hetflejš J., Holý A., Rosenberg I.: Czech. 229 088.
23. Niebergall H.: Makromol. Chem. *52*, 218 (1962).
24. Čapka M.: Synth. React. Inorg. Met.-Org. Chem. *7*, 347 (1977).
25. Czakoová M., Čapka M.: J. Mol. Catal. *11*, 313 (1981).
26. Kinting A., Čapka M., Krause H. W.: J. Mol. Catal. *33*, 215 (1985).
27. Bažant V., Chvalovský V., Rathouský J.: *Organosilicon Compounds*, Vol. 1, p. 59. Academia, Prague 1965.
28. Schraml J., Čapka M., Jancke H.: Collect. Czech. Chem. Commun. *47*, 793 (1982).
29. Zbirovský V., Kreuzfeld H. J., Čapka M.: React. Kinet. Catal. Lett. *29*, 243 (1985).

30. Černý M., Collect. Czech. Chem. Commun. *42*, 3069 (1967).
31. Reissová A., Čapka M.: Synth. React. Inorg. Met.-Org. Chem. *16*, 707 (1986).
32. Čapka M.: Czech. 252 619.
33. Čapka M.: Czech. 257 226.
34. Čapka M., Hetflejš J.: Collect. Czech. Chem. Commun. *39*, 154 (1974).
35. Čapka M., Hetflejš J., Rosenberg I., Holý A.: Czech. 228 065 (1984).
36. Porsch B., Rosenberg I., Čapka M.: Czech. 234 939.
37. Noll W.: *Chemie und Technologie der Silicone*. Verlag Chemie, Weinheim 1968.
38. Čapka M., Selke R.: J. Mol. Catal., in press.
39. Selke R., Burneleit H., Čapka M.: Ger. (GDR) 2525/8929/DD (1989).
40. Kozák K., Čapka M.: Collect. Czech. Chem. Commun. *44*, 2624 (1979).
41. James B. R.: *Homogeneous Hydrogenation*. Wiley, New York 1973.
42. McQuillin F. J.: *Homogeneous Hydrogenation in Organic Chemistry*. Reidel, Dordrecht 1976.
43. Jakoubková M., Čapka M.: Collect. Czech. Chem. Commun. *45*, 2219 (1980).
44. Čapka M.: Kinet. Katal. *23*, 291 (1982).
45. Čapka M., Schraml J., Jancke H.: Collect. Czech. Chem. Commun. *43*, 3343 (1978).
46. Broučková Z., Czakoová M., Čapka M.: J. Mol. Catal. *30*, 241 (1985).
47. Mestroni G., Camus A., Zassinovich G. in: *Aspects of Homogeneous Catalysts* (R. Ugo, Ed.), p. 71. Reidel, Dordrecht 1980.
48. Rylander P.: *Catalytic Hydrogenation in Organic Synthesis*. Academic Press, New York 1979.
49. Pukhnarevich V. B., Burnashova I. D., Omelchenko G., Dukhanskaya I. I., Čapka M., Voronkov M. G.: Zh. Obshch. Khim. *56*, 2092 (1986).
50. Heidingsfeldova M., Čapka M.: J. Appl. Polym. Sci. *30*, 1837 (1985).
51. Michalska Z. M., Čapka M., Stoch J.: J. Mol. Catal. *11*, 323 (1981)).
52. Michalska Z. M.: J. Mol. Catal. *3*, 125 (1977/78).
53. Nefedov W. I.: Coord. Khim. *4*, 1283 (1978).
54. Adams D. M., Chandler P. J.: J. Chem. Soc., A *1969*, 588.
55. Čapka M., Hetflejš J., Vdovin V. M., Fedorov V. E., Pritula N. A., Fedorova G. K.: React. Kinet. Catal. Lett. *31*, 41 (1986).
56. Čapka M.: Collect. Czech. Chem. Commun. *42*, 3410 (1977).
57. Osborn J. A., Jardine F. Hö, Young J. F., Wilkinson G.: J. Chem. Soc., A *1966*, 1711.
58. Strucul G., Bonivento M., Graziani M., Cernia E., Palladino N.: Inorg. Chim. Acta *12*, 15 (1975).
59. Pinno P., Bonivento M., Strucul G., Braziani M., Cernia E., Palladino N.: J. Mol. Catal. *1*, 309 (1975/76).
60. Zbirovský V., Čapka M.: Collect. Czech. Chem. Commun. *51*, 836 (1986).
61. Čapka M. in: *Homogeneous and Heterogeneous Catalysis* (Y. Yermakov and V. Likholobov, Eds). Science Press, Utrecht 1986.
62. Reiss J., Hetflejš J.: Collect. Czech. Chem. Commun. *51*, 340 (1986).
63. Nacomber D. W., Hart W. P., Rausch M. D.: Adv. Organomet. Chem. *21*, 1 (1982).
64. Wild F. R. W. P., Gubitosa G., Britzinger H. H.: J. Organomet. Chem. *148*, 73 (1978).
65. Jackson R., Rudelsen J., Thomson D. J., Whelan: J. Organomet. Chem. *125*, 57 (1977).
66. Reissová A., Bastl Z., Čapka M.: Collect. Czech. Chem. Commun. *51*, 1430 (1986).
67. Čapka M., Reissová A.,: Collect. Czech. Chem. Commun. *54*, 1760 (1989).
68. Bažant V., Čapka M., Dietzmann I., Fuhrmann H., Hetflejš J., Pracejus H.: Czech. 199 329.
69. Čapka M., Vozka S.: Czech. 253 842.
70. Tříska J., Ulík R., Vodička L., Janda V., Čapka M.: J. High. Resolut. Chromatogr., Chromatogr. Commun. *11*, 222 (1988).
71. Čapka M., Vozka S.: Czech. 257 650.

72. Čapka M., FuhrAann H.: Czech. 170 439.
73. Schomaker E., Zarteveen A. J., Challa G., Čapka M.: J. Polym. Sci. *29*, 157 (1988).
74. Čapka M., Czakoová M., Čermák J., Sufčák M., Reiss J.: Czech. Appl. 3758—89.
75. Hjorkjaer J., Heindrich B., Čapka M.: Appl. Organomet. Chem. *4*, 369 (1990).
76. Evans D., Osborn J. A., Wilkinson G. J.: Chem. Soc., A *1968*, 1133.
77. Čapka M., Svoboda P., Hetflejš J.: Czech. 154 469.
78. Kavan V., Čapka M.: Collect. Czech. Chem. Commun. *45*, 2100 (1980).
79. Osborn J. A., Jardine F. H., Young H. F., Wilkinson G.: J. Chem. Soc. *1966*, 1711.
80. Kagan H. B. in: *Comprehensive Organometallic Chemistry* (G. Wilkinson, F. G. A. Stone and E. V. Abel, Eds), Vol. 8, p. 163. Pergamon Press, Oxford 1982.
81. Hetflejš J. in: *Catalytic Hydrogenation* (L. Červený, Ed.), p. 497. Elsevier, Amsterdam 1986.
82. Selke R.: React. Kinet. Catal. Lett., in press.
83. Čapka M., Hetflejš J., Selke R.: React. Kinet. Catal. Lett. *10*, 225 (1979).
84. Beneš J., Hetflejš J.: Collect. Czech. Chem. Commun. *41*, 2264 (1976).
85. Naaktgeboren A. J., Nolte R. J. M., Drenth W.: Am. Chem. Soc. *1980*, 102.
86. Selke R.: J. Mol. Catal. *37*, 227 (1986).
87. Selke R., Pracejus H.: J. Mol. Catal. *37*, 213 (1988).
88. Špaček M., Vozka S., Rosenberg I.: Czech. 249 610.
89. Nagel U., Kinzel E.: J. Chem. Soc., Chem. Commun. *1986*, 1098.
90. Zemanová I., Turková J., Čapka M., Nakhpetyan L. A., Švec P., Kálal J.: Enzyme Microb. Technol. *3*, 229 (1981).
91. Stratilová E., Čapka M., Rexová-Ber.ková L.: Biotechnol. Lett. *9*, 511 (1987).
92. Fusek M., Čapka M., Turková J.: Biotechnol. Lett. *9*, 561 (1987).
93. Rexová-Benková L., Stratilová E., Čapka M.: Biocatalysis, in press.
94. Ivanov A. S., Turková J., Čapka M., Zubov V. P.: Biocatalysis *3*, 235 (1990).
95. Stratilová E., Čapka M., Rexová-Benková L.: Biocatalysis *2*, 317 (1989).

Translated by J. Hetflejš.