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Heterogeneous Metal Complex Catalysts

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The review is devoted to methods of synthesis and catalytic properties of heterogeneous metal complex catalysts in which the selectivity and activity of homogeneous metal complexes and the technological advantages of traditional heterogeneous catalysts are combined. The adsorption and chemical interactions between the transition metal complexes and solid carriers (organic and mineral) are discussed and the activities and selectivities of heterogeneous metal complex catalysts and their homogeneous analogues are compared. Studies published up to 1976 are considered.
The bibliography includes 203 references.

CONTENTS

I.	Introduction	751
II.	Adsorption binding of transition metal complexes	752
III.	The binding of transition metal complexes by ion-exchange resins	753
IV.	π-Coordination of transition metal complexes to polymeric phosphino-macroligands	753
V.	The binding of transition metal complexes to other polymeric macroligands	758
VI.	Conversion of transition metal complexes into heterogeneous systems on mineral carriers	759
VII.	Incorporation of metal complexes in polymer gels	762

I. INTRODUCTION

We are witnessing a vigorous growth of research in the field of homogeneous metal complex catalysis. Catalysis by transition metal complexes (TMC) is finding an increasing number of new applications as regards both theoretical and applied aspects: oxidation of hydrocarbons, stereospecific polymerisation, homogeneous hydrogenation, hydroformylation, and fixation of molecular nitrogen. This is by no means a complete list of the fields in which metal complex catalysts are used. However, although they have definite advantages over the traditional heterogeneous catalysts (high overall activity and selectivity), homogeneous catalysts suffer from significant disadvantages: their application requires the introduction into the process of a stage in which the reaction products and the catalyst are separated. The difficulty of isolating the catalyst from the reaction mixture and the difficulties associated with its reuse are responsible for the relatively small contribution of homogeneous catalytic processes to industry. The only exception is the polymerisation process in which the catalyst remains incorporated in the high-molecular-weight compound, which, incidentally, has an undesirable influence on the quality of the latter.

There is no doubt that in the foreseeable future heterogeneous catalysis will become dominant in industrial processes. Consequently catalytic systems involving heterogeneous catalysts based on transition metal complexes will be vigorously developed. Catalysts of this kind have come to be referred to as "hybrid"; it is believed that they are capable of ensuring the high selectivity and activity characteristic of homogeneous metal complexes and the technological usefulness characteristic of traditional heterogeneous catalysts. The development of studies in this field is hindered by the inadequacy of the theoretical ideas concerning the nature of the action of hybrid catalysts. For example, the problems of the influence of ligands on the catalytic activity of the metal ion, of the dependence of the catalytic activity on the carrier structure and on the number of transition metal atoms in the active centre, and the possibility of the occurrence of reaction on metal complexes in the absence of a solvent, etc. remain unsolved. A number of reviews have been devoted[1-16] to the synthesis and properties of heterogeneous catalysts obtained as a result of the conversion of transition metal complexes into heterogeneous formations on mineral and polymeric carriers.

Commereuc and Martino[13] suggest that heterogeneous catalytic systems be classified on the basis of three features: (1) the type of initial compound containing the transition metal atom; (2) the method used to activate the heterogeneous system; (3) the nature of the carrier-matrix. Although such classification is undoubtedly useful, it does not provide any information about the nature of the bond between the TMC and the carrier, which is very important from the standpoint of both the stability of the hybrid catalyst obtained and the interpretation of the results. Heterogeneous metal complex catalysts can be divided into the following types in terms of the nature of the bonds between the TMC and the carrier: (1) adsorption fixation of the TMC on the carrier; (2) binding of the TMC by ion-exchange resins; (3) π-coordination of the TMC on the carrier, which plays the role of a macroligand; (4) σ-binding of the TMC by the functional groups of the carrier; (5) the incorporation of the TMC in polymer gels.

It is readily seen that the methods used to convert the TMC into heterogeneous systems have much in common with those for the immobilisation of enzymes[17]. The main difficulty arising in the formation of heterogeneous systems from TMC is that the catalytic activity of the complex is caused either by the presence of a weakly bound ligand in the coordination sphere or the presence of a free coordination site. The interaction of the TMC with the carrier usually occurs via this "weak unit", which inevitably entails a loss of catalytic activity.

We shall consider below various methods for the conversion of the TMC into heterogeneous systems, noting, incidentally, the nature of the catalytic activity and, wherever possible, comparing the hybrid catalysts with their homogeneous analogues.

II. ADSORPTION BINDING OF TRANSITION METAL COMPLEXES

The first studies on the conversion of TMC into heterogeneous systems were concerned with the physical adsorption of such complexes on mineral carriers[18-23]. The general principle underlying the preparation of catalytic systems of this kind may be considered in relation to the study of Acres et al.[18] The familiar homogeneous isomerisation catalyst[24-26] $RhCl_3.3H_2O$ was dissolved in ethylene glycol and the resulting solution was added to a suspension of silica gel in methanol; after the removal of methanol, the catalyst showed a high activity in the isomerisation of pent-1-ene. Using the same method, Rony[21,27] compared the $(PPh_3)_2Rh(CO)Cl/SiO_2$ catalyst, which propagates the hydroformylation of propene. A similar catalytic system was prepared by Bond[28], who deposited the complex $RhH(CO)(PPh_3)_3$ on silica gel.

The study of the influence of the conditions of the catalytic process on the properties of the catalyst showed that four complexes converted into heterogeneous systems on a mineral carrier [$RhCl_3$ in the isomerisation reaction and $(PPh_3)_2Rh(CO)Cl$, $(AsPh_3)_2Rh(CO)Cl$, and $Co_2(CO)_6(PBu_3)_2$ in the hydroformylation reaction] are more active in the liquid-phase process, while Wilkinson's catalyst $(PR_3)_3$. .PhCl is more active under the conditions of a gas-phase process[29].

TMC have been deposited on mineral carriers also by controlled adsorption from the gas phase. Vasserberg and coworkers[30] prepared a nickel–alumina catalyst by the adsorption of nickel tetracarbonyl on alumina at a reduced pressure. After reduction with hydrogen (at 400° C for 12 h), the activity of the specimen was investigated in the reduction of carbon dioxide to methane and proved to be higher than that of specimens with the same amount of metal but obtained by precipitation or by impregnation of silica gel with nickel salts. This result can probably be accounted for by the significantly higher degree of dispersion of the metallic nickel obtained from the carbonyl.

A catalyst for the disproportionation of propene,

$$2C_3H_6 \rightarrow C_4H_8 + C_2H_4$$

has been obtained[31] from molybdenum hexacarbonyl. The authors found that the degree of reaction is highest in the range 290–340° and were also able to show that the active centre is the complex $Mo(CO)_x(C_3H_6)_{6-x}(x = 3,4)$.

The catalysts obtained by the deposition of $Mo(CO)_6$ on oxide carriers have also been studied[32-34]. Later investigations yielded more precise data on the nature of the active centres of deposited catalysts based on molybdenum hexacarbonyl[35,36] and the influence of poisons on their activity[37]. It is noteworthy that, when transition metal carbonyl compounds are adsorbed on oxide carriers, physical adsorption does not occur in all cases. Parkyns' study[38] of the interaction of nickel carbonyl with silica gel and alumina showed that, whereas the usual physical adsorption is observed on the former carrier, on the latter the vibration frequencies of the CO group in the infrared spectrum correspond to the vibrations of carbon monoxide adsorbed on nickel.

A number of studies have been made recently on the conversion of carbonyl cluster complexes into heterogeneous systems on mineral carriers[39-42]. The most interesting study[42] is that undertaken to compare the catalytic activities of the complexes Cp_2Ni, $Cp_2Ni_2(CO)_2$, and $Cp_3Ni_3(CO)_2$ ($Cp = \pi\text{-}C_5H_5$) "heterogenised" on silica gel. The nickel catalysts obtained by the decomposition of adsorbed complexes *in vacuo* at 80–120° C showed significant differences in their catalytic properties. Thus the catalyst obtained by the decomposition of nickelocene adsorbed on silica gel is active in the trimerisation of acetylene to benzene, unlike cluster systems. On the other hand, the H_2–D_2 exchange reaction and the hydrogenation of ethylene and benzene take place much more readily in the presence of polynuclear catalysts, while the hydroformylation reaction occurring in the presence of cluster catalysts does not take place at all in the presence of specimens obtained by the decomposition of adsorbed nickelocene.

The use of cluster compounds in catalysis opens new pathways in the formation of highly selective catalysts as well as catalysts capable of propagating structurally hindered processes[41,42]. From the standpoint of the theory of catalysis, a detailed study of such systems will make it possible to determine the structures of the active centres of traditional catalysts in various processes.

Catalysts based on cobalt, copper, silver, and platinum have been obtained by impregnating mineral carriers with TMC solutions[43-45]. A study of the low-temperature conversion of carbon monoxide over the CuO/SiO_2 and CuO/Al_2O_3 catalysts established that[43] specimens obtained from the amminecopper complex exhibit a higher activity than those obtained by impregnating alumina and silica gels with copper nitrate. Comparison of the catalytic activities[46] of the $RhCl_3.3H_2O/C$(act.) and Rh_2O_3/C(act.) systems[47] in the carbonylation of methanol

$$CH_3OH + CO \xrightarrow[CHI_3(ind.)]{} CH_3COOH$$

yielded a similar result[46]. By studying the kinetics of this reaction in the presence of the $RhCl_3.3H_2O/C$(act.) catalyst and by comparing them with those of the homogeneous catalytic carbonylation of methanol in the presence of the free rhodium complex, the authors[46] found that the process mechanisms are the same in the two instances.

An interesting method of synthesis of hybrid adsorption catalysts was proposed by Mochido et al.[48] Using the Cu(II)–Y zeolite, obtained by ion exchange in an ammonia solution, as the carrier, they treated it in one case with ethylenediamine (EDA) and in another with dimethylglyoxime (DMG). The study of the infrared spectra showed that copper chelate complexes are formed with the organic reagents; the systems can be represented as Cu–DMG/Cu–Y and Cu–EDA/Cu–Y. The authors[48] studied the catalytic properties of the specimens in the decomposition of hydrogen peroxide and established that one complex molecule on the surface decomposes approximately 400 H_2O_2 molecules. It was observed that the activity of the Cu–EDA/Cu–Y catalyst is five times higher than the activity of the zeolite untreated with EDA; on the other hand, the Cu–DMG/Cu–Y specimen exhibits a lower activity than the initial zeolite.

A comparative study of the dimerisation of propene in the presence of homogeneous and heterogeneous catalytic systems incorporating nickel acetylacetonate and an organoaluminium compound has been carried out[49,50]. The authors were able to show that the adsorption of the catalyst on porous mineral carriers with a high specific surface leads not only to an increase of the stability of the action of the catalysts, but also to an increase of their thermal stability.

In conclusion of this Section one should note that a common deficiency of the adsorption methods for the conversion of TMC into heterogeneous systems is the low strength of the bond between the physically adsorbed complex and the carrier, which leads to the elution of the TMC

from the carrier surface during the reaction. Furthermore, physical adsorption may entail the formation of polymolecular TMC layers, which lowers the efficiency of the active compound and may cause agglomeration of the complex, which also reduces the efficiency.

III. THE BINDING OF TRANSITION METAL COMPLEXES BY ION-EXCHANGE RESINS

The interaction of a cation-exchange resin with acid sodium tungstate led to the synthesis of a catalyst for the oxidation of maleic acid[51,52]:

$$\equiv N^+Cl^- + NaHWO_4 \rightarrow \equiv N^+HWO_4^- + NaCl\ .$$

A number of carbonylation, hydrogenation, and hydroformylation catalysts, obtained by the conversion of Group VIII transition metal complexes into heterogeneous systems on ion-exchange resins, have been patented[53-60]. Thus a method has been described[55] for the preparation of catalysts based on $[Pd(NH_3)_4]^{2+}$ with low- and high-molecular-weight counterions; the former catalysed the interaction of allyl chloride with carbon monoxide in a homogeneous system and the latter catalysed the same reaction in a heterogeneous system:

$$CH_2{=}CH{-}CH_2Cl + CO \rightarrow CH_2{=}CH{-}CH_2COCl\ .$$

It was found that both catalysts exhibit comparable activities and selectivities in the above reaction.

Hanson and coworkers[61,62] prepared hybrid catalysts using a sulphonated styrene–divinylbenzene copolymer containing sodium phosphinate groups as the ion exchanger. They investigated the reduction of the catalysts by hydrogen and hydrazine after the interaction of the ion exchangers with ammine complexes of platinum, palladium, nickel, and silver and the catalytic activities of the resulting catalysts in the oxidation of ethanol. A similar study has been made[63-66] using hydroxylated Amberlite A-27 as the carrier. The $PdCl_4^{2-}$/A-27, $RhCl_6^{3-}$/A-27, and $Pd(PPh_3)_4^{2+}$/A-27 catalysts, which are active in the hydrogenation of unsaturated compounds, were obtained.

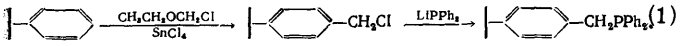
Berenblyum and coworkers[67-70] obtained an effective hybrid catalyst for the hydrogenation of olefins on the basis of a new water-soluble complex $NaH_3[(acac)Rh(O_2)_2.Rh(OH)(H_2O)]$, by converting it into a heterogeneous system on an ion-exchange resin containing amino-groups.

Hybrid catalysts obtained by converting metal complex ions into heterogeneous systems on ion exchangers have an important advantage over physically adsorbed TMC, which consists in a greater binding strength. A disadvantage of these heterogeneous hybrid catalysts is the impossibility of using them to prepare uncharged complexes, particularly zero-valent complexes, which are widely used.

IV. π-COORDINATION OF TRANSITION METAL COMPLEXES TO POLYMERIC PHOSPHINO-MACROLIGANDS

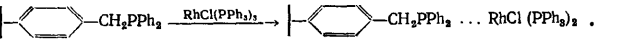
Manassen[5] suggested that the catalytic activities of free TMC and TMC bound to a polymer chain should exhibit differences due to the orientation of the polymeric ligand, steric hindrance, and the change in the stability constant of the complex. According to Patchornik and Kraus[71], the bond between a TMC and a stereoregular insoluble polymer restricts the motion of the active centre on the surface; if the distance between the active centres is sufficiently large, it is possible to achieve a dilution such that they do not interact with one another. The rate of reaction should be higher in this case than in the usual homogeneous catalysis, because, according to the authors[71], catalyst molecules in solution lose part of their energy as a result of mutual collisions. Having adopted this view, one must suppose that fixation on the carrier promotes an increase of the activity of homogeneous catalysts. However, as will be shown below, this is by no means always the case.

The most frequently used polymeric carrier for conversion into heterogeneous systems by coordination is the styrene–divinylbenzene copolymer containing the diphenylphosphine group. This carrier-macroligand is synthesised as follows[72-76]:



(1)

The presence of phosphino-groups in the polymer makes it possible to coordinate the TMC to the phosphorus atom. Thus a number of workers[73,77-81] converted the familiar homogeneous Wilkinson's catalyst[82] into a heterogeneous system on a phosphinated styrene–divinylbenzene copolymer, having replaced one of the triphenylphosphine ligands in each molecule of the complex by the polymer-diphenylphosphino-group of the carrier:



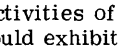
Their method involves the establishment of equilibrium between the TMC converted into the heterogeneous system and the TMC in the inert solvent from which the complex is deposited; at room temperature such equilibrium is established in 2–4 weeks[73].

The study of the catalytic activity of the catalyst thus prepared in the hydrogenation of olefins demonstrated a significant dependence of the reaction rate on the size of the substrate molecules. While the relative rates of hydrogenation w of hex-1-ene, 2-cholestene, octadecene, cyclo-octene, and cyclododecene on the homogeneous Wilkinson's catalyst are comparable, when the hybrid catalyst is used, they (w') differ strongly:

Olefin	Cyclohexene	Hex-1-ene	Δ^2-Cholestene	Octadecene	Cyclo-octene	Cyclododecene
w'	1.00	2.55	0.03	0.50	0.40	0.23
w	1.00	1.40	0.71	0.71	1.00	0.67

Thus it follows from the above investigation[73] that the conversion of a homogeneous catalyst into a heterogeneous system makes it possible to increase significantly its selectivity while retaining its high overall activity.

Analogous catalytic systems based on the styrene–divinylbenzene copolymer and different phosphine and chloride complexes of rhodium have been investigated[83,84]. The authors studied the possibility of using hybrid catalysts in hydroformylation and hydrosilylation reactions in addition to hydrogenation. By varying the low-molecular-weight ligands at the rhodium atom, the authors were able to choose catalysts for the selective hydrogenation of hept-1-ene, having almost completely excluded the parallel reaction involving the migration of the double bond. The

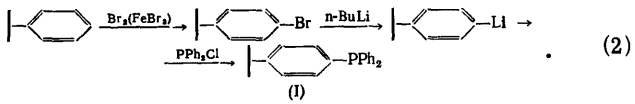
catalyst —  $CH_2PPh_2...RhCl_X$ proved to be highly

active in the hydrogenation reaction. An analogous catalyst had been obtained somewhat earlier[55].

Active hydroformylation catalysts were prepared by the above procedure from dicarbonylrhodium acetylacetonate and cobalt carbonyl[85,86]. The study of their catalytic activity in the hydroformylation of olefins[85] showed that they ensure 99% selectivity of conversion into an aldehyde for an overall degree of reaction of 87%.

Using Haag and Whitehurst's method[53], Bruner and Bailar[87,88] prepared a carrier based on the chloromethylated Amberlite HAD-4, containing benzyldiphenylphosphino-groups on the surface. Palladium and platinum chloride complexes were then coordinated to the phosphorus atom. The resulting catalysts were investigated in the hydrogenation of polyunsaturated hydrocarbons, and it was established that, for example, the palladium–polymer catalyst is extremely active in the selective hydrogenation of such hydrocarbons to mono-olefins. In addition, it has been found[87] that the hydrogenation of conjugated diene hydrocarbons proceeds faster than that of non-conjugated compounds. The platinum–polymer catalyst exhibits an activity under more severe conditions and its use requires the obligatory presence of tin chloride in proportions of Pt : Sn = 1 : 10.

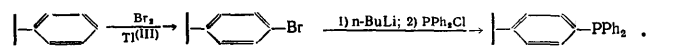
Yet another method of synthesis of the polymer matrix has been proposed by Collman and coworkers[89]:



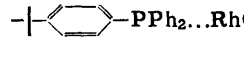
(2)

An advantage of this method is the possibility of grafting the diphenylphosphino-groups directly to the benzene rings of the styrene–divinylbenzene polymer. The reaction of compound (I) with $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ yields polynuclear heterogeneous metal-complex catalysts. Collman et al.[89] showed that hybrid catalysts having the general formula $MClL_3$ (where M = Rh or Ir and L = I) are more active than their homogeneous analogues.

The above method has been modified[90] by brominating the benzene rings of the polymer in the presence of thallium(III) ions:

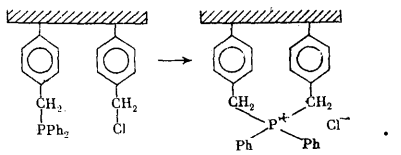


The authors[90] then coordinated Wilkinson's catalyst and obtained a hybrid hydrogenation catalyst. The degree of binding of the complex to the polymer in the above study[90] was 0.53 mmole g^{-1}, which is somewhat less than in the study of Collman et al.[89] The composition of the active centre may be represented by the formula

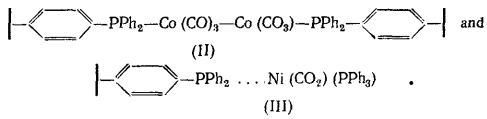


$-PPh_2...RhCl(PPh_3)_2$. By comparing the activities of the hybrid catalyst with Wilkinson's catalyst, the authors[90,91] established the following characteristics of the hydrogenation of olefins: (1) olefins with a terminal double bond are hydrogenated faster than those containing a double bond within a carbon chain; (2) *cis*-olefins are hydrogenated faster than the *trans*-isomers; (3) olefins are hydrogenated faster than acetylenes. The dependence of the rate of hydrogenation of two double bonds in conjugated cyclic dienes on the ring size (cyclo-octa-1,3-diene > cyclohexa-1,3-diene) was demonstrated, that for the hybrid catalyst being significantly more pronounced than for the homogeneous catalyst. The authors[90] also studied the appreciable difference between the ratio of the *cis*- and *trans*-isomers of *p*-menthanes obtained by the hydrogenation of 1,(7)-*p*-menth-1(7)-ene. Thus the ratio is 2.0 : 1 for tris-triphenylphosphinerhodium chloride, while for the hybrid catalyst it amounts to 3.1 : 1, i.e, in this case the use of the hybrid catalyst entails a shift towards a higher selectivity.

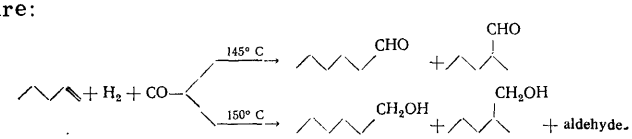
A hybrid catalyst based on the phosphinerhodium complex fixed on a polystyrene macroligand has been synthesised by Mitchell and Whitehurst[92]. The catalyst was found to have a low activity in the hydroformylation reaction, which the authors explain by the presence on the polymer surface of a quaternary phosphorus atom which is incapable of coordinating the transition metal:



The activities of hybrid and homogeneous catalysts have also been compared in studies[7,93] where cobalt and nickel complexes grafted to the styrene–divinylbenzene copolymer were synthesised and investigated:

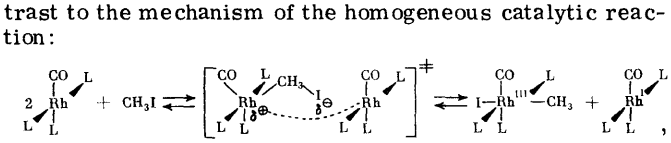


The former proved to be active in the isomerisation and hydroformylation reactions and the latter proved to be active in the cyclo-oligomerisation reaction. It is noteworthy that at high pressures the selectivity of the hydroformylation reaction is effectively regulated by temperature:



The hydroformylation of pent-1-ene has been studied[94] in the presence of the TMC $RhCl(CO)(PPh_3)_2$ and $RhH(CO).(PPh_3)_3$, converted into heterogeneous systems on a styrene–divinylbenzene matrix containing surface phosphino-groups. It was found that the catalytic activity and selectivity of the hybrid catalysts are the same as those observed for their homogeneous analogues.

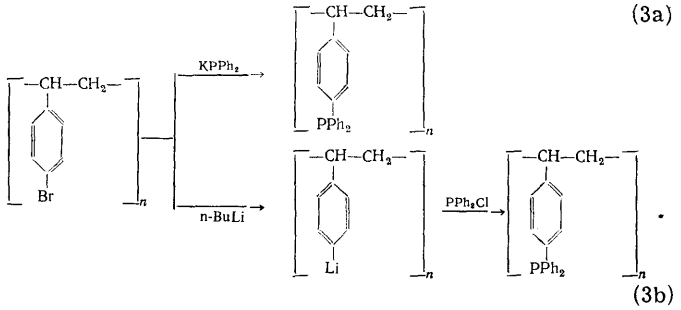
In the general case the mechanisms of the action of the homogeneous and the corresponding hybrid catalysts are presumably the same, since the natures of their active centres are the same. However, it has been shown in relation to the carbonylation of methanol in the presence of the $RhCl(CO)(PPh_3)_2$ complex bound to a polymer[95] that the mechanisms of the homogeneous and heterogeneous catalytic reactions may differ. The difference was manifested by the change of the first order of the reaction with respect to rhodium to the second (for the hybrid catalyst), while the reaction was of zero order with respect to methanol and carbon monoxide and of first order with respect to methyl iodide (playing the role of a promoting agent) in reactions of both types. In view of their results, the authors[95] suggested that two rhodium centres are involved in the rate-limiting stage of the reaction in contrast to the mechanism of the homogeneous catalytic reaction:



where L are polymeric and low-molecular-weight ligands which were not detected in the active form of the complex. According to this mechanism, the carbon of the CH_3I group undergoes nucleophilic attack by Rh(I) in the complex acting as a Lewis base; the second Rh(I) centre acts as a

Lewis acid, stabilising the transition state. This mechanism explains (although not completely) the possibility of the stereochemical formation of a transition state of this kind.

A large series of studies on the conversion of TMC into heterogeneous systems on polymeric carrier-macroligands containing phenylphosphino-groups have been carried out by Allum and coworkers[96-100], who showed[96] that, depending on the method of synthesis of the polymeric macroligand, it is possible to vary within wide limits the number of phosphino-groups fixed on the polymer. Thus, after treatment with potassium phenylphosphide, the polymer obtained by polymerising *p*-bromostyrene in the presence of benzoyl hydroperoxide contains 3.4 wt.% of phosphorus. A polymer containing 6 wt.% of phosphorus is obtained on synthesis via mechanism (3b), analogous to that proposed by Collman et al.[89] [see reaction (2) above]:

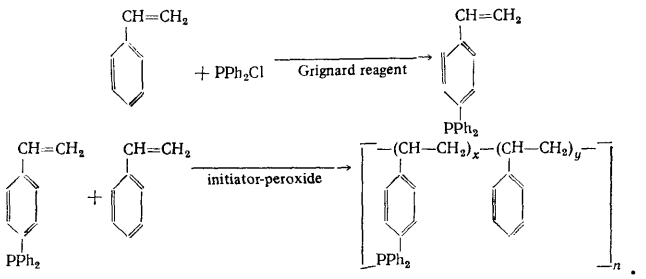


(3a)

(3b)

A somewhat smaller number of surface phosphino-groups is obtained in the synthesis of the matrix via reaction (1). In this case the polymer contains 4–5 wt.% of phosphorus.

A polymeric polystyrene matrix containing phosphino-groups can be obtained[5,93] by the polymerisation of *p*-diphenylphosphinostyrene[5,93]:



The preparation of other polymeric carrier-macroligands, suitable for the synthesis of hybrid catalysts and containing phosphino-groups, has been described[96-100]; poly(vinyl chloride), polychloroprene, polybutadiene, poly(vinyl alcohol), and other polymers have been used. Phosphino-groups were introduced into the first two polymers by direct reaction with $KPPh_2$. The phosphorus contents were respectively 11 and 3 wt.%. After preliminary treatment with hydrogen bromide, polybutadiene was treated with potassium diphenylphosphide, which yielded a product containing 6–8 wt.% of phosphorus. A phosphinated polybutadiene can also be obtained by the interaction of the initial polymer with diphenylphosphine under the influence of ultraviolet light[98]. Chlorodiphenylphosphine and dichlorophenylphosphine were used as phosphinating agents in the study with poly(vinyl alcohol). In the first case the polymer contained 1.7 and in the second 6–7 wt.% of phosphorus[96]. The authors suggest that the bond between phosphorus and carbon is formed via oxygen. The ready hydrolysability of this bond limited the practical application of the carrier. Nevertheless the above matrix makes it possible to employ phosphite groups in the conversion of TMC into heterogeneous systems.

Table 1. The composition of heterogeneous transition metal complexes.

Initial polymer	Polymeric ligand *P*, wt.%	TMC for conversion into heterogeneous form	
		TMC	metal, wt.%
Poly-*p*-bromostyrene	5.9	$CoCl_2$	0.7
Non cross-linked polystyrene	4.7	$CoCl_2$	4.3
Cross-linked polystyrene	4.35	$CoCl_2$	2.8
Amerlite HAD-2	2.0	$Ni(C_8H_{12})_2$	0.3
Amberlite HAD-2	2.0	$Rh(acac)(CO)_2$	2.0
Amberlite HAD-2	2.2	$[RhCl(C_8H_{12})]_2$	2.7
Poly-(vinyl chloride)	4.3	$CoCl_2$	4.6
Poly-(vinyl chloride)	4.75	$Rh(acac)(CO)_2$	7.3
Polybutadiene	7.9	$CoCl_2$	3.1

Table 1 presents the compositions of a series of heterogeneous TPM obtained by Allum et al.[96] It is noteworthy that complete information about the catalytic activity is available only for the TMC made heterogeneous on Amberlite, because only such hybrid catalysts are completely insoluble in the reaction media. It was found that the proportions of the phosphino-groups of the macroligand and the heterogeneous TMC may influence significantly the rate of the catalytic process. Thus the catalytic activity of a fixed iridium complex has been compared[101] with that of the analogous homogeneous catalyst in the hydrogenation of cyclo-octa-1,5-diene (1,5-COD) and the result shows that for P :Ir = 1 :1 the degree of conversion of 1,5-COD in the presence of the polymer-bound catalyst is greater than for P :Ir < 5 (Table 2). The lower rate of the heterogeneous reaction compared with the homogeneous process for large P :Ir ratios was explained[101] by the low mobility of the heterogeneous complex.

The influence of temperature on the catalytic activity of the hybrid catalyst was also noted[101]. The ratio of the activities at 170° and 80°C changed from 0.8 to 5 over the entire range of phosphorus contents in the polymer (from 1.91 to 10.28 wt.%). For a homogeneous catalyst, the ratio is always greater and lies in the range 8–10. Assuming the same mechanism of the catalytic activity over the entire temperature range, the authors explain this effect by the high mobility of the diphenylphosphino-groups fixed on the polymer.

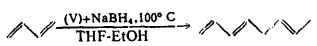
Thus it becomes evident that, in the study of the properties of hybrid catalysts containing a carrier-macroligand and when they are compared with homogeneous analogues, it is necessary to take into account factors such as the concentration and mobility of the surface-active groups responsible for the coordination of the TMC. This creates additional difficulties in comparing hybrid and homogeneous catalysts and in simulating catalysts with specified properties.

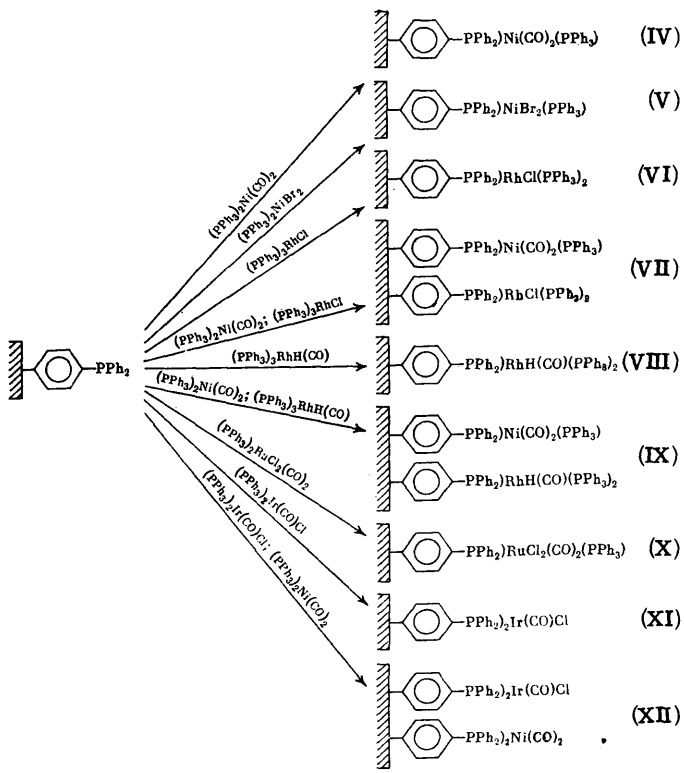
The studies of Pittman and coworkers[102,105] on the preparation of hybrid catalysts which propagate a sequential multistep catalytic process are of considerable interest. The idea of devising such catalysts was put forward by Mossbach[106], who immobilised simultaneously hexokinase and glucose-6-phosphate isomerase on polystyrene and achieved the sequential conversion of glucose, initially

into glucose-1-phosphate and then into glucose-6-phosphate. Thus the product of the first enzymatic reaction became the substrate of the second. Pittman and coworkers attempted to apply this concept to "heterogenised" TMC. In order to elucidate the nature of the influence of different "heterogenised" TMC on one another, catalysts were prepared[102] by the joint coordination of different metal complexes on a polystyrene–divinylbenzene copolymer containing phosphino-groups and by mixing catalysts prepared beforehand; the hybrid catalysts investigated are listed below.

The oligomerisation of buta-1,3-diene was the model reaction in the studies of Pittman and coworkers. The data obtained for the activity of catalyst (IV) and the proportions of the reaction products were satisfactorily reconciled with those obtained earlier[107,108] for the activity of the homogeneous $(PPh_3)_2Ni(CO)_2$ catalyst. The complete correspondence of the homogeneous-catalytic reaction to the heterogeneous-catalytic process was explained[102–105] by the absence of steric hindrance for the small molecule of the diene hydrocarbon.

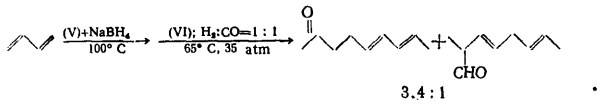
Catalyst (V), reduced by two equivalents of $NaBH_4$ to give polymer-bound zero-valent nickel, retained 90% of its activity and proved to be highly selective (98%) in the linear dimerisation of buta-1,3-diene[109]:





This result is inconsistent with data obtained in a study of the activity of the homogeneous $(PPh_3)_2NiBr_2$ catalyst[110], in the presence of which a whole series of products are obtained.

When catalyst (V) modified by sodium tetrahydroborate is mixed with catalyst (VI), an active catalyst, which selectively oligomerises and hydroformylates buta-1,3-diene, is obtained:



The combination of the oligomerising catalyst (IV) with the hydrogenating catalyst (VI), which has been suggested as catalyst (VII) on a common matrix, proved to be successful:

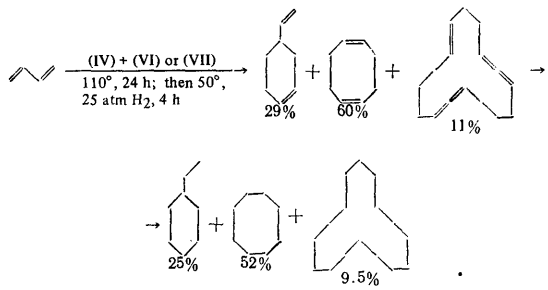


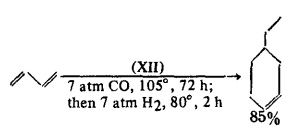
Table 2. Comparison of the rates of hydrogenation of 1,5-COD in the presence of the hybrid and homogeneous $Ir(CO)Cl(PPh_3)_2$ catalysts in benzene (170° C; 10 atm).

Catalyst	P:Ir	Total *P* content on polymer, wt.%	Time, h	Conversion	
				cyclooctene, %	cyclooctane, %
Homogeneous	3	—	33	37	3
Hybrid	3	4.02	0.25	57	4
Homogeneous	4	—	48	44	3
Hybrid	4	10.28	0.25	69	5
Homogeneous	6	—	72	68	11
Hybrid	7	4.02	93	5	0
Hybrid	7	1.25	0.20	68	6
Homogeneous	14	—	72	50	1
Hybrid	12	2.53	94	19	2
Hybrid	12	4.02	96	6	0
Homogeneous	22	—	72	15	0
Hybrid	22	4.02	93	18	2

By employing different version of hybrid catalysts based on $(PPh_3)_2Ni(CO_2)_2$ and $(PPh_3)_2RuCl_2(CO)_2$ [(IV) + (X)], it proved possible to obtain mono-olefins with a high degree of selectivity via the oligomerisation stage. It is noteworthy that homogeneous catalysts propagate the process analogously under the same conditions.

By varying different catalysts, Pittman and coworkers[102] obtained complete and partial hydrogenation, oligomerisation, and hydroformylation products from buta-1,3-diene, and the hybrid catalyst, obtained on a common matrix and carrying two different catalytically active groups, propagated the process in the same way as the catalyst obtained by mixing two complexes made heterogeneous separately.

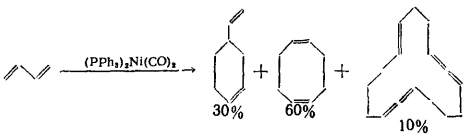
The observation of the process



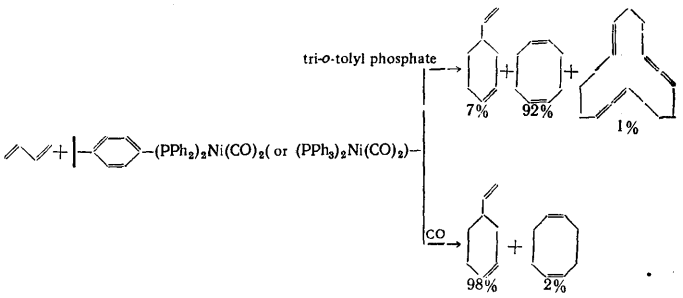
which occurs on catalyst (XII) with high yields, must be recognised as one of the most important results obtained [102].

The attainment of a high selectivity of the hybrid catalysts which propagate a consecutive multistage catalytic process increases significantly the effectiveness of such systems; this explains the attention which Pittman and coworkers [109,111,112] devoted to the preparation of selective oligomerisation and hydrogenation catalysts.

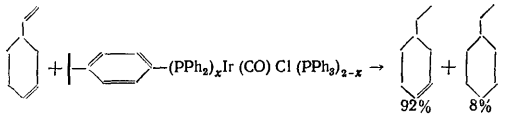
Conditions under which butadiene selectively dimerises either to 4-vinylcyclohexene (4-VCH) or to cyclo-octa-1,5-diene have been described [111]. The proportions of the butadiene oligomerisation products in the presence of the $(PPh_3)_2Ni(CO)_2$ homogeneous catalyst may be represented as follows [107,108]:



The promotion of this homogeneous catalyst or its "heterogenised" analogue by carbon monoxide or phosphite may alter significantly the selectivity of the catalytic system:

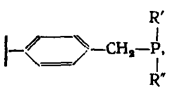


A catalyst capable of the selective propagation of the hydrogenation stage—the Vasko's complex "heterogenised" on a phosphinated styrene–divinylbenzene copolymer, i.e.

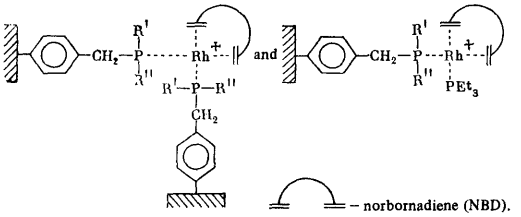


has been proposed [111] and the possibilities of this selective hydrogenation catalyst have been studied in detail [111,112].

By varying the substituents at the phosphorus atom of the polymer matrix, Graziani and coworkers [113,114] attempted to obtain a high selectivity of a hybrid phosphino-polymer catalyst, on which a transition metal complex had been deposited, in the hydrogenation of the double bond and the carbonyl group:



where R′ = R″ = Ph, or R′ = Me and R″ = Ph, or R′ = menthyl and R″ = Ph. The rhodium complexes [Rh(NBD).(acac)] and $[Rh(NBD)(PEt_3)_2]^+$ were fixed on the surface of the matrix, which resulted in the formation of the following catalysts:

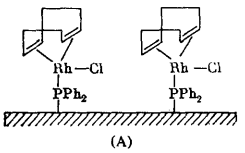


These deposited catalysts proved to be selective in the hydrogenation of the carbonyl group and the double bond of the olefin. It was noted [113,114] that the increase of the basicity of the phosphine coordinated to the rhodium atom increases the activity of the catalyst in the reduction of the carbonyl group, diminishing at the same time its activity in the hydrogenation of the olefin. It is noteworthy that in the study of the reduction reaction certain results may be partly distorted owing to the presence of the liberated metal.

Dumont et al. [115] investigated yet another ketone conversion reaction—catalytic hydroxylation. The hybrid catalyst consisted of a rhodium(I) complex "heterogenised" on a complex polymer matrix. The effectiveness of this catalytic system proved to be very similar to that of the corresponding homogeneous system. The possibility of repeated utilisation of the heterogeneous catalyst was noted as its main advantage.

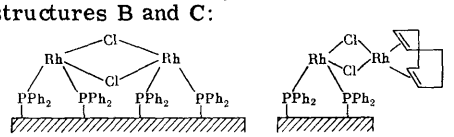
In conclusion we shall examine the structure of the active centres in the hybrid catalysts obtained. When complexes are "heterogenised" there is a possibility of two types of binding, in the first of which the phosphinated polymer plays the role of a monodentate macroligand, and in the second it chelates the TMC. It is noteworthy that this question is not as yet entirely clear.

Thus, on "heterogenising" the same complex $[RhCl(COD)]_2$ on phosphinated polystyrene, Collman et al. [89] and Grubbs et al. [116] reached different conclusions concerning the nature of the binding of the transition metal to the polymeric macroligand. According to Collman et al., [89] when this complex is "heterogenised" on cross-linked (to the extent of 2%) polystyrene, the process reduces to the rupture of a Cl bridge, and the formation of the adduct



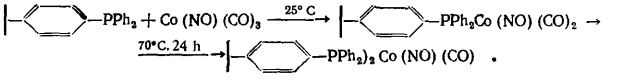
(A)

Grubbs et al. [116] established that, when the complex is "heterogenised" on a polymer with the same degree of cross-linking, two moles of COD are liberated per mole of the TMC, which may be represented by the surface structure B. For higher degrees of cross-linking of the polymer (20%), the way in which the rhodium complex is rendered heterogeneous alters, since 1.4 moles of cyclo-octadiene are evolved per mole of the adsorbed compound, which can be accounted for by the formation of the set of surface structures B and C:



(B) (C)

A study of the coordination of carbonyl TMC on phosphinated polystyrene matrices established[89,93] that, although in the majority of cases chelation by the carrier takes place, in certain cases a mixed type of coordination occurs [for example, when the complex $Rh_4(CO)_{12}$, to the active centres of which the structure $|-\langle\rangle-(PPh_2)_{1.5}\cdot Rh_4(CO)_{10.5}$ has been attributed, is made heterogeneous[80]] as well as monodentate binding, which may be transformed into chelate binding under more severe conditions[89]:



Collman et al.[89] also described the possibility of tridentate binding of the complex $RhCl(PPh_3)_2(CH_2=CH_2)$ by the polymeric macroligand, which leads to the formation of a complete polymeric analogue of Wilkinson's complex.

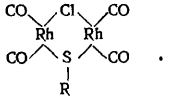
Thus one may conclude that the structure of the surface centres in the "heterogenised" complexes may depend on (1) the nature of the polymer, the structure of its surface group, and the degree of cross-linking, (2) on the composition and structure of the "heterogenised" transition metal complex, and (3) on the conditions under which the complex is "heterogenised".

V. THE BINDING OF TRANSITION METAL COMPLEXES TO OTHER POLYMERIC MACROLIGANDS

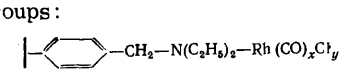
The preparation of hybrid catalysts based on polymers with phosphino-groups was examined above. Attempts have been made to achieve the coordination of the complex also to other groups.

The conversion of olefins into aldehydes and alcohols in the presence of rhodium-containing complexes on *p*-substituted polystyrenes, where the substituents were $-N(CH_3)_2$, $-CH_2N(CH_3)_2$, $-P(C_4H_9)_2$, $-CH_2PPh_2$, or $-SH$, has been studied[117] and it has been found that the hybrid catalysts and their homogeneous analogues have approximately the same selectivities in the formation of aldehydes. The phosphinerhodium complexes exhibited a very high selectivity in the formation of an aldehyde, while the aminerhodium complexes showed a high selectivity in the formation of an alcohol. On the other hand, the activity of the hybrid amino-catalyst in the above reaction proved to be much higher than that of its homogeneous analogue.

The cleavage of the dimeric rhodium complex $[Rh(CO_2)Cl]^2$ by monomeric amines and phosphines has been investigated[118]. When the complex was rendered "heterogenised" on a polymer, a hybrid catalyst propagating the hydrogenation and hydroformylation reactions was formed. The study of the influence of monomeric and polymeric thiols on the cleavage of the heterogeneous complex showed that monomeric thiols do not cleave the complex molecule, giving rise to $[Rh(CO)_2RS]_2$, while polymeric thiols yield a product having the following structure:



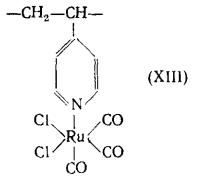
Mitchell and Whitehurst[92] rendered a rhodium carbonyl complex heterogeneous on a polystyrene polymer containing ethylamino-groups:



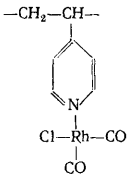
The catalyst thus obtained showed a very low activity in the hydrogenation of methyl linoleate, but exhibited an exceptionally high selectivity in the selective hydrogenation of a single double bond: it propagates the hydrogenation of terminal double bonds significantly faster than that of inner double bonds.

Moffat's studies[119,120] led to new possibilities in the employment of finished polymers as matrices for the fixation of transition metal complexes in order to obtain hybrid catalysts. When cobalt carbonyls were made heterogeneous on poly-2-vinylpyridine, it proved possible to obtain an active hydroformylating system and it was established that only approximately 40% of the nitrogen atoms of the polymeric carrier are capable of participating in complex formation with cobalt carbonyl. The hydroformylation of hex-2-ene in the presence of such a system at 165–170°C takes place to the extent of 50% (p = 124 atm, $H_2:CO = 1:1$).

Braca et al.[121] prepared a hybrid catalyst by attaching the complexes $[RuCl_2(CO)_3]_2$ and $[RhCl(CO)_2]_2$ to linear poly-4-vinylpyridine (P4VP):

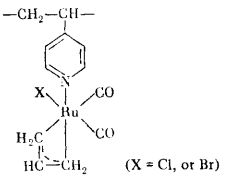


(XIII)



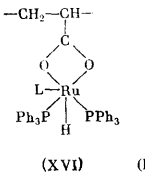
(XIV)

However, the metal-polymer complex catalysts obtained proved to be relatively inactive and operated only under very severe conditions. Thus the first of two catalysts (XIII), used in the synthesis of ethers from propene, CO, and methanol, propagated the process at 30 atm and 190°C. Under these conditions, the complex was rapidly split off from the polymeric matrix and the polynuclear complex $Ru_3(CO)_{12}$ was formed[122]. In an attempt to obtain a higher activity of a hybrid ruthenium complex catalyst, the authors[123,124] fixed the $RuCl(\pi\text{-}C_3H_5)(CO)_3$ and $RuBr(\pi\text{-}C_3H_5)(CO)_3$ complexes[123,124] to P4VP and the complex $RuH_9(PPh_3)_3L$ (where L = PPh_3 or CO) to polyacrylic acid:



(X = Cl, or Br)

(XV)



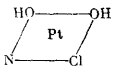
(XVI)

(L = PPh_3, or CO)

The hybrid catalyst (XV) proved to be active under relatively mild conditions (100°C) in many reactions employing unsaturated hydrocarbons as substrates (for example, in the isomerisation of but-1-ene), the complex remaining attached to the polymer under the reaction conditions. By comparing the activities of hybrid complexes (XV) with their homogeneous analogues in the isomerisation of but-1-ene, Braca et al.[121] established that, while their selectivity remains the same, the activity of the catalysts deposited on the polymer is in many cases higher than that of the homogeneous TMC. In the isomerisation and hydrogenation of pent-1-ene in the presence of complex (XVI) the hybrid catalyst is significantly less active than its homogeneous analogue, which the authors attributed to the steric hindrance to the reaction arising in the presence of the polymeric catalyst.

A whole series of catalysts for the hydrosilylation of alkenes, alkynes, and alkadienes, active in liquid and gaseous phases, have been prepared [84,125-129] by "heterogenising" certain TMC (for example chloroplatinic acid and tetracarbonylrhodium dichloride) on styrene–divinylbenzene copolymers with surface dimethylamino- and cyano-groups.

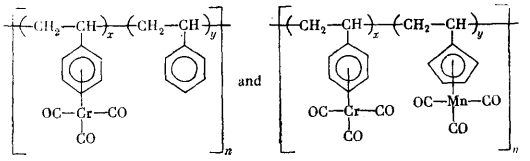
Studies of the catalytic properties of platinum, iridium, rhodium, and palladium chloride complexes deposited on nylon (where the transition metal atom is coordinated to the nitrogen atom of the peptide group in nylon) in the hydrogenation of benzene established [130-132] that, in order to obtain an active catalyst, the presence of a hydroxy-group in the coordination sphere of the complex is necessary. The structure of the catalytically active platinum complex obtained by depositing H_2PtCl_6 on nylon is [130]



When the catalytic activities of metal–nylon complexes with respect to benzene hydrogenation products, referred to 1 gram-atom of the metal, are compared, the metals can be arranged in the following sequence: Ir > Pt > Rh > Pd. [132]

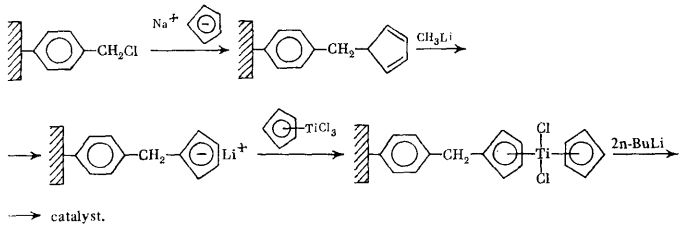
One must note that the hydrogenation of metal-complexes on a polymeric support does not always lead to the formation of a hybrid catalyst. Thus Kraus and Tomanova [133], who attached $PdCl_2$ to a styrene–divinylbenzene copolymer containing $-CH_2-CN$ surface groups, did not obtain a catalyst active in relation to olefins.

Transition metal complexes can be bound to a polymeric matrix by a procedure other than via heteroatomic groups specially introduced into the polymer and coordinating the transition metal. For example, by employing the benzene rings of polystyrene as a π-coordinating agent and synthesising polymers with a specified structure, Pittman and coworkers [124,125] obtained complexes having the following composition:

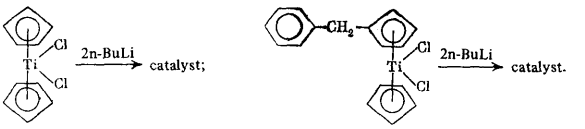


The first catalytic system proved to be active in the selective hydrogenation of methyl sorbate to methyl-3-hexenoate in cyclohexane at 160°C and 35 atm. [134]

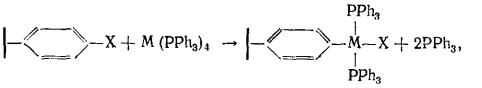
Grubbs et al. [116] synthesised a styrene–divinylbenzene copolymer with attached titanocene, which was thus made heterogeneous:



This system proved to be six times more active in the hydrogenation of cyclohexene than the corresponding homogeneous catalytic systems:



Mizoroki et al. [136] proposed a new method for converting transition metal complexes into heterogeneous systems on a polymer by the formation of a σ-bond between the transition metal atom and a carbon atom in the polymeric matrix. This approach is based on studies [137-139] in which σ-aryl complexes of nickel, palladium, and platinum were obtained by the oxidative addition of an aryl halide to the corresponding tetrakis(triphenylphosphine) complexes of transition metals. The reaction with halogenated polystyrene was carried out as follows [140]:



where M = Ni, Pd, or Pt and X = Br or I.

The complexes prepared in this way were treated with boron trifluoride etherate in the presence of small amounts of water and were investigated as catalysts of the dimerisation of ethylene and propene [136,141]. The former reaction was studied using the catalyst in the liquid phase and the latter was studied in the vapour phase in the presence of a hybrid catalyst—activated by BF_3OEt_2/H_2O (in proportions of 10 : 1). As regards the nature of the catalytic activity, these systems are identical with their low-molecular-weight analogues, although their activities are somewhat lower.

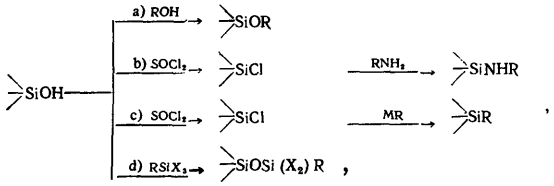
VI. CONVERSION OF TRANSITION METAL COMPLEXES INTO HETEROGENEOUS SYSTEMS ON MINERAL CARRIERS

The employment of polymeric carriers in order to convert TMC into heterogeneous systems makes it possible to apply a wide variety of synthetic methods. However, all the above catalysts suffer from one common disadvantage: the polymeric base of the systems is responsible for their low thermal stability and low resistance to the action of oxidants. Mineral carriers are free from this disadvantage. Studies dealing with the deposition of TMC on mineral carriers can be divided into two groups: (1) conversion into a heterogeneous system via a coordination reaction using organosilicon compounds as agents fixing the TMC to the surface; (2) conversion of TMC into heterogeneous systems directly on the mineral carrier via the functional groups of the latter.

The most widely used mineral carrier is coarsely porous silica gel subjected to preliminary hydroxylation, although it has been stated [142-144] that alumina gel and crystalline and amorphous aluminosilicates have been used to "heterogenise" TMC.

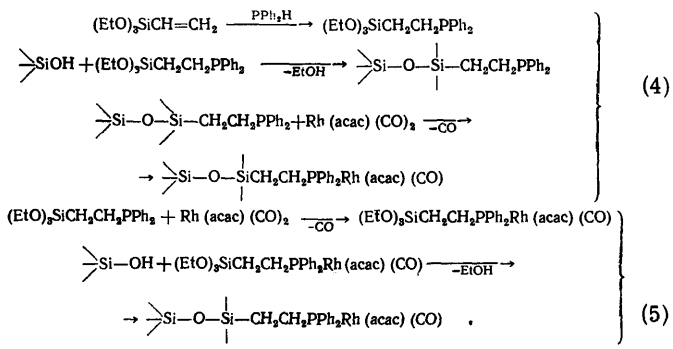
1. Conversion into Heterogeneous Systems Using Organosilic Compounds

Functional groups can be grafted to silica gel in several ways:



where R is an organic hydrocarbon group, X a readily hydrolysable group such as Cl, OR, or OCOR, and MR an organometallic compound such as LiR or XMgR. The synthesis of macroligands for hybrid catalysts by methods (a)–(c) has not been described in the literature, but there are data concerning the preparation of a carrier for TMC by method (d), which is probably due to the greater thermal stability and greater resistance to hydrolysis of the Si–C bond compared with those of the Si–O–C and Si–N–C linkages. Furthermore, the attachment of the functional group by method (d) can be readily achieved in a single stage under mild conditions and makes it possible to employ a large set of modifying agents.

The investigations of Allum and coworkers [145–153] of the preparation of hybrid catalysts based on silanised silica gel must be regarded as the first studies of this kind. Such catalysts are synthesised in accordance with the following schemes [145,149]:



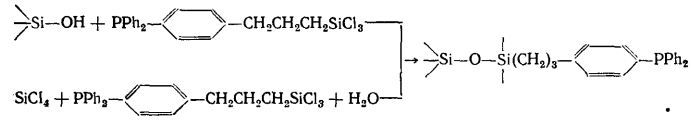
(4)

(5)

It is noteworthy that not only the rhodium acetylacetonate complex but also other rhodium, palladium, and platinum complexes may be converted into heterogeneous systems [152].

The catalysts prepared in this way were used in hydrogenation and hydroformylation processes [145,150], but their activity was somewhat lower than that of the corresponding low-molecular-weight analogues. By "heterogenising" other transition metal complexes, the limits of the applicability of such heterogeneous catalysts are expanded and they can be used for the isomerisation and acetoxylation of olefins, for the oligomerisation of dienes, for the polymerisation and cyclo-oligomerisation of acetylenes [149], and for the hydrosilylation of olefins [151–153]. Apart from the phosphino-group, the following "anchor" groups have been used: $-CH_2CH_2CN$, $-CH_2CH_2CH_2NH_2$, $-CH_2CH_2CH_2NEt_2$, $-CH_2CH_2CH_2SH$, $-CH_2CH_2CH_2CH_2-C_6H_4-N$, $-C_6H_4-CH_2N(CH_2PPh_2)_2$, and $-CH_2CH_2CH_2N$ [150–152].

Moreto et al. [90] prepared a phosphine-containing silica gel matrix to which they subsequently coordinated $RhCl(PPh_3)_3$ and $[RhCl(C_2H_4)_2]_2$:



The study of the catalytic activity of rhodium complexes fixed on a phosphinated silica gel support in the hydrogenation of *p*-menth-1(7)-ene showed that the ratio of the *cis*- and *trans*-*p*-menthanes obtained in the reaction is 9.2 : 1, which indicates a higher selectivity of the catalyst compared with homogeneous Wilkinson's catalyst and the rhodium complex "heterogenised" on polystyrene (see Section IV) [90].

Thus one may claim that in many instances a fairly high process selectivity may be achieved on synthesising hybrid catalysts by coordinating TMC to a phosphinated silica gel.

Comparison of the catalytic activities of complexes "heterogenised" on a phosphinated polymer and on a mineral carrier, which makes it possible to estimate the influence of the support on the catalytic properties of the systems, is of great interest. The data of Michalska and Webster [154], who established that the rate of hydrogenation of pent-1-ene in the presence of $RhH(CO)(PPh_3)_3$ attached to a phosphinated silica gel is six times higher than in the presence of a complex bound to a polystyrene matrix, provides one of the few examples of such a comparison. The authors [154] explained this effect, which has been observed also by other investigators [80,103], by the hindered diffusion of the substrate molecules to the active centres within the polymer pores. Furthermore, they established [154] that the activities of the complex $RhH(CO)(PPh_3)_3$ "heterogenised" on silica gel and its homogeneous analogue are virtually indistinguishable. The rates of hydrogenation of pent-1-ene are in proportions of 1.3 : 1.4. Similar results were also obtained in another investigation [80].

We believe that the similarity in the behaviour of catalysts "heterogenised" on silica gel and the homogeneous catalysts can be explained by the fact that the silicon–hydrocarbon support to which the complex is attached creates conditions for the additional mobility of the active centre, as a result of which the properties of the "heterogenised" complex on a mineral support approach those of the homogeneous complex and differ from the complex bound to a polymer.

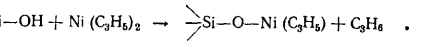
2. Conversion into a Heterogeneous System with Formation of a σ-Bond between the Transition Metal and the Carrier

The disadvantages of the preparation of hybrid catalysts by the method described above include the large number of stages in the synthesis and its long duration as well as insufficient stability of the bond between the TMC and the matrix. These disadvantages may be eliminated by the direct interaction of TMC with the mineral carrier, which results in the formation of stable σ-bonds between the central metal atom and the carrier.

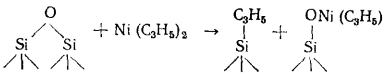
The first studies in this field include those described in Refs. 155–158. Here we shall only mention that, by modifying the surface of aluminosilicate with tris-π-allylchromium, Shmonina and Stefanovskaya prepared a catalyst which proved to be active in the *trans*-1,4-polymerisation of butadiene and isoprene. Subsequently the

copolymerisation of butadiene and isoprene was achieved in the presence of the same catalytic system [159,160].

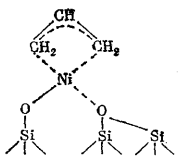
Detailed systematic studies have been made on the structures and catalytic activities of catalysts obtained by modifying mineral carriers with π-allyl complexes of transition metals [158,161-170,172-187]. A general method for the preparation of such catalysts has been examined in relation to the fixation of bis-π-allylnickel in the presence of silica gel [158,173]:



It was shown that this is the main type of binding, involving the elimination of one propene molecule, although at a higher concentration of the organometallic compound or in the presence of silica gel heated at a higher temperature, binding to the oxygen groups of the carrier is possible (see also Skupinsky and Malinovski [188]):



Square coordination obtains in a surface organonickel complex:



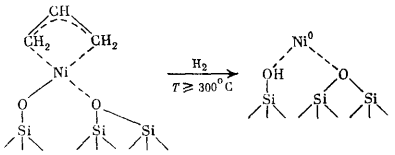
Ermakov et al. [161] established an interesting feature of the π-allyl linkage in the surface complex. They found that, in terms of a number of properties, it differs significantly from the linkage in bis-π-allylnickel, being thermally more stable, but at the same time showing a greater tendency towards hydrolysis. Thus the heterogeneous complex reacts with water at 20°C to give propene.

It has been shown [158] that surface compounds may be used as catalysts of different processes in three states.

1. In the initial state, i.e. directly after treating the carrier with the π-allyl complex. Such surface coordination compounds can serve as active centres in the polymerisation of olefins and dienes [162-164,166,167] and the disproportionation of olefins (propene) [168,169,184]. Comparison of the catalytic activities of hybrid catalysts with those of their homogeneous analogues showed that, whereas bis-π-allylnickel [170] and tetrakis-π-allylmolybdenum [171] do not induce the polymerisation of butadiene, the allyl complex of nickel deposited on silica gel gives rise selectively to the *cis*-1,4-polymer, $Ni(C_3H_5)_2/Al_2O_3$ produces the *trans*-1,4-polymer, while $Mo(C_3H_5)_4$ deposited on carriers gives rise to a polymer having a mixed structure. Furthermore, butadiene is known to polymerise in the presence of π-allylnickel halides with the preferential formation of the *trans*-1,4-polymer [172], while the π-allylnickel halide system on silica gel induces *cis*-1,4-polymerisation [162].

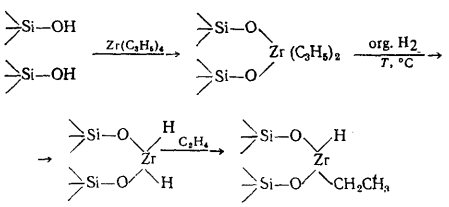
Thus one may claim that hybrid catalysts are more capable of increasing significantly the activity and of altering the selectivity, compared with their homogeneous analogues.

2. In the reduced state, where the low-valence state of the transition metal atom is stabilised by the surface groups of the carrier. The reduction of the surface allyl complex of nickel is described by the scheme



It is of interest that the stabilisation of nickel atoms by the oxygen atoms of the silica gel matrix is so pronounced that it protects them from further agglomeration to large crystals. This follows from data obtained in a study of the magnetic susceptibilities of specimens of nickel catalysts [158]. The catalysts obtained in the reduced state proved to be active in hydrogenation reactions [158,173], while a deposited and reduced molybdenum complex was active in ammonia synthesis [174].

An interesting study has been made on the stabilisation of highly dispersed platinum on silica gel (obtained after the deposition and reduction of π-allyl complexes) by molybdenum prepared similarly. The formation of Pt–Mo clusters has been suggested and then proved by X-ray photoelectron spectroscopy; such clusters protects the platinum atoms from further migration and agglomeration to form crystals [180,183]. A catalyst of the polymerisation of ethylene, whose structure and the mechanism of its action have been determined mass-spectrometrically, has been prepared in the reduced state by depositing tetrakis-π-allylzirconium on silica gel [175,176]:



3. A hydrogen oxidation catalyst has been prepared in the oxidised state [165]:



Not only allyl complexes of transition metals but also their chloride complexes have been "heterogenised" [166]; the $TiCl_3/SiO_2$ catalyst proved to be active in the polymerisation of ethylene. Studies [189,190] on the polymerisation of ethylene on "heterogenised" cyclopentadienyl, arene, and allyl complexes of chromium are closely related to those of Ermakov and coworkers [165,166]. Zhorov and coworkers [191, 192] employed the same approach as Ermakov and coworkers [165,166] and deposited benzonitrilepalladium complexes on silica gel. In their earlier study of the activity of these compounds in homogeneous systems [193,194] they had established that the complex $(PhCN)_2PdCl_2$ is exceptionally active in the migration of the double bond and that the addition of methanol appreciably accelerates this reaction. A significant disadvantage of the introduction of methanol into the system is rapid decomposition of the complex with liberation of metallic palladium.

Zhorov et al. [191] established that the complex attached to silica gel is 100 times more active in the isomerisation of pent-1-ene than its homogeneous analogue and that the

introduction of methanol into the heterogeneous system does not affect its activity. The results led to the hypothesis that the deposition results in the formation of the stable complex $\geq$Si-O-PdClLL′ or $\geq$Si-O-PdClL$_2$ (where L′ = benzonitrile and L = labile olefin ligand), while in the presence of methanol added to the homogeneous system, unstable compounds having the composition CH_3O-PdClL$_2$ are formed.

The study of the activities of hybrid catalysts demonstrated a distinct maximum at a specific metal complex concentration, which was explained by an optimum amount of $(PhCN)_2PdCl_2$ for hydrogenation, above which the reaction

$$2L'_2PdCl_2 + 2L \rightarrow (LPdCl_2)_2 + 4L',$$

takes place, and the benzonitrile liberated as a result competes in coordination, lowering the overall activity of the catalyst.

It is noteworthy that the results of Zhorov et al.[191] require further confirmation, since only exact data on the structure of the surface groups make it possible to demonstrate unambiguously the structure of the catalyst.

Another approach was used by Lisichkin and coworkers[195-198] in the preparation of hybrid catalytic systems, the essential feature of which is that complexes of nickel bound to a Group IVA element are used as the organometallic compounds:

$$(CpLNi)_xM^{IV}Cl_{4-x} \xrightarrow[-NH_4Cl]{NH_3,\ CH_3OH} (CpLNi)_xM^{IV}(OCH_3)_{4-x} \xrightarrow{\equiv Si-OH} \rightarrow (CpLNi)_xM^{IV}(OCH_3)_{4-x-y}\left(OSi\equiv\right)_y,$$

where L = PPh_3, PBu_3, or CO, M^{IV} = Si, Ge, or Sn, x = 1 or 2, and y = 1, 2, or 3. The strength of the Ni–M^{IV} and M^{IV}–O bonds is responsible for the absence of the aggregation of nickel atoms on the silica gel surface up to 250°C. Treatment of the fixed complexes with hydrogen at an elevated temperature leads to partial elimination of the ligands and to the appearance of catalytic activity.

Since tin and germanium can combine not only with one but also with two nickel atoms, Lisichkin et al.[198] were able to compare the activities of mono- and di-atomic nickel centres in the hydrogenation of olefins. It was found that catalysts with diatomic centres are not only more active but also more stable.

By varying the nature of the ligands at the nickel atom, it was possible to alter specifically the selectivity of the catalysts. Thus it was shown[197] that the usual impregnated nickel catalyst, modified with triphenylphosphine, exhibits the same selectivity as the triphenylphosphine-nickel complex fixed on silica gel.

VII. INCORPORATION OF METAL COMPLEXES IN POLYMER GELS

In 1971, Kabanov[199] suggested that the catalytic systems consisting of grains of polymer gels in the bulk phase of which the corresponding active centres are immobilised be used as catalytic systems. A characteristic feature of such catalysts is the possibility of the occurrence of reactions not only on the surface of the grain, but also throughout the bulk of the swollen polymer particle. In such systems the effectiveness of the utilisation of the active centres should be just as high as in heterogeneous catalysts. At the same time the reaction products should be readily removable from the catalytic gel.

Subsequently Kabanov and coworkers[200] undertook a series of studies devoted to the formation of metal complex gel-like polymerisation catalysts. They showed that catalysts of this type exhibit a high stability, polymerising, for example, ethylene at elevated temperatures up to 200°C, i.e. under conditions where the usual catalysts of the Ziegler–Natta type are deactivated very rapidly. After the catalyst had been used for 2000 h, virtually no decrease of activity was observed. The yield of the polymer after this period may reach up to 500 kg per gram of the transition metal. It is extremely significant that the polyethylene obtained in the presence of gel-like catalysts contains virtually no transition metal compounds, i.e. does not require washing. Each catalyst grain consists in essence of a tiny reactor from which the polymer formed diffuses to the surrounding solution, while the metal compounds forming part of the composition of the active centre remain firmly bound inside.

The use of catalytic systems of this kind requires, however, particular attention to processes involving the diffusion of the reaction product from the gel-like particle. Clearly, in the synthesis of polymer molecules with a high molecular weight the reaction rate begins to be limited by the rate of diffusion.

The literature data presented in this review show that the "heterogenised" TMC are likely to be very useful in catalysis. Despite the fact that there is still a long way to go before a detailed understanding of the action of deposited metal catalysts is achieved, certain important conclusions may already be made.

Fixation of TMC on mineral and polymeric carriers to form heterogeneous systems makes it possible to retain to a large extent the activity and selectivity of the corresponding homogeneous catalysts.

In many instances conversion into heterogeneous systems, makes it possible to increase significantly the activity of the homogeneous catalyst owing to the greater stability of the coordination-unsaturated state of the transition metal atom on the surface and the absence of agglomeration of the active particles.

Conversion of TMC into a heterogeneous form gives rise to great possibilities for the development of catalysts with the structure of active centres specified beforehand by varying the nature of the metal, the mode of binding to the carrier, the nature of the ligand, etc.

The improvement of methods for the conversion of TMC into heterogeneous systems will apparently make it possible to synthesise heterogeneous catalysts with complex but entirely identical active centres, i.e. to solve the problem of the formation of catalysts the selectivity of the action of which is similar to that of enzymes.

During the period when the manuscript was with the editors, numerous new studies devoted to "heterogenising" TMC on both organic and mineral carriers were published. A fairly complete list of publications on the "heterogenisation" of TMC up to the middle of 1977 is given in the bibliographic guide published by the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences[201]. The great interest of investigators in the problem of the synthesis and study of hybrid catalysts is indicated by the proceedings of the conferences held in Novosibirsk (June, 1977)[202] and Lyons (November, 1977)[203]. One can apparently conclude that heterogeneous metal complex catalysis is one of the principal fields in which modern catalytic chemistry will develop.

Analysis of studies published recently shows that the following main trends have arisen: (1) the synthesis of hybrid catalysts without homogeneous analogues; (2) the development of methods of synthesis of bi- and polyfunctional catalysts; (3) the use of organometallic compounds for the synthesis of highly dispersed deposited metallic catalysts; (4) the conversion of metal complex cluster compounds into a heterogeneous form.

One should bear in mind that the possibilities of catalysis by transition metal complexes fixed on a surface have been by no means fully utilised. The use of hybrid catalysis containing a fixed chiral centre has given rise to considerable possibilities for asymmetric catalytic synthesis.

There have been virtually no studies concerning the application of metal complex catalysis to processes which can be achieved only at elevated temperatures. The use of stable "heterogenised" complexes on mineral carriers will make it possible to solve this problem.

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