Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymer Effect on Catalysis by Macromolecules/Transition Metal Complexes

Francesco Ciardelli[a]; Carlo Carlini[b]; Paolo Pertici[c]; Giorgio Valentini[c]
[a] Dipartimento di Chimica e Chimica Industriale, Universitá di Pisa e Centro Macromolecole Stereordinate ed Otticamente Attive, Pisa, Italy [b] Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna, Bologna, Italy [c] Dipartimento di Chimica e Chimica Industriale, Università di Pisa e Centro Macromolecole Stereordinate ed Otticamente Attive, Pisa, Italy

To cite this Article Ciardelli, Francesco , Carlini, Carlo , Pertici, Paolo and Valentini, Giorgio(1989) 'Polymer Effect on Catalysis by Macromolecules/Transition Metal Complexes', Journal of Macromolecular Science, Part A, 26: 2, 327 — 347
To link to this Article: DOI: 10.1080/00222338908051977
URL: http://dx.doi.org/10.1080/00222338908051977

J. MACROMOL. SCI.–CHEM., A26(2 & 3), pp. 327-347 (1989)

POLYMER EFFECT ON CATALYSIS BY MACROMOLECULES/TRANSITION METAL COMPLEXES[†]

FRANCESCO CIARDELLI*

Dipartimento di Chimica e Chimica Industriale
Università di Pisa e Centro Macromolecole Stereordinate ed
Otticamente Attive
CNR
Via Risorgimento 35, 56100 Pisa, Italy

CARLO CARLINI

Dipartimento di Chimica Industriale e dei Materiali
Università di Bologna
Viale del Risorgimento 4, 40136 Bologna, Italy

PAOLO PERTICI and GIORGIO VALENTINI

Dipartimento di Chimica e Chimica Industriale
Università di Pisa e Centro Macromolecole Stereordinate ed
Otticamente Attive
CNR
Via Risorgimento 35, 56100 Pisa, Italy

ABSTRACT

The present status of research in the field of macromolecules/transition metal complexes is critically reviewed on the basis of selected examples both from the authors' laboratories and other laboratories around the

---

[†] Dedicated with deep sorrow to the memory of Professor Horst Pracejus who prematurely left the Scientific Community, which regarded him among its outstanding members.

world. The substantial lack of inertness of the polymeric ligand (the polymer effect) is examined and shown to occur in most cases during preparation of the macromolecule/transition metal complex as well as during its catalytic use. This behavior is attributed and confirmed as due to the polydentate ligand character of the macromolecules and to the effect of physical and chemical parameters which can be varied over large ranges. Future work is duscussed for the development of the field in suitable directions.

1. INTRODUCTION

It is now well established and generally accepted that organic macromolecules can often act as ligands for transition-metal complexes, thus affecting structure and catalytic properties of the resulting systems. Indeed, macromolecules are better viewed as ideal ligands for preparing hybrid catalysts that combine the good properties of homogeneous and heterogeneous systems, rather than inert supports for heterogenizing soluble complexes.

Both crosslinked and linear organic and inorganic polymers have been largely used in the last few decades for heterogenizing transition-metal catalysts. These supports can be functionalized to give ligands for attaching transition-metal complexes through coordinate bonds as in the corresponding soluble monomeric analogs. The main goal of this approach was the preparation of catalytic systems displaying the good activity, selectivity, and reproducibility typical of homogeneous catalysts, combined with the easy separability and recovery characteristic of heterogeneous catalysts [1-3]. However, a limited number of reactions exists using macromolecular ligands in the same way as the corresponding monomeric analogs. In most cases, in fact, the close vicinity of binding groups in polymer ligands gives rise to different interactions with the transition-metal complex, with formation of different active sites and consequent decrease of reaction selectivity. The main factors to be taken into account for controlling the reaction and obtaining species with definite structure have been identified, but the applicability of reliable preparative strategies is still limited to a few actual situations.

When the structure of metal centers coordinated to the polymer is the same as in the monomer, the large steric hindrance by the polymer matrix reduces the catalytic activity that is only partially attenuated by the swelling or dissolving of the systems with a proper liquid medium. This aspect suggests that the macromolecular ligand, in contrast to a traditional inert support, can modify catalytic behavior by physically interacting with solvent media and thus modulating the reaction rate.

In addition, the macromolecular matrix can affect the selectivity and stereoselectivity, both from steric and geometrical origin. The former is observed when the macromolecular ligand produces a specific steric environment around the metal centers in the active sites and can take place either in solution or in heterogeneous systems. Some typical examples are known, but more work should be done in this context.

A very special and useful application of this last concept is the preparation of catalysts for asymmetric synthesis either by using optically active polymer ligands or by fixing optically active metal complexes on polymer matrices [4, 5].

Shape selectivity can be achieved, on the other hand, in the heterogeneous phase with metal complexes supported on crosslinked polymers, where the dimension of pores has been controlled by modulating the degree and type of crosslinking.

In some cases the rigidity of the macromolecular ligand due either to its molecular structure or to proper design of the network structure can provide a useful method to stabilize reactive intermediates, thus allowing their isolation and identification. This type of heterogenized systems can then provide information on the mechanism of the same reaction carried out with the corresponding homogeneous catalysts, giving labile nonisolable intermediates. Moreover, the improved stability of active species helps to achieve catalytic systems capable of maintaining their activity during recycling.

The most attractive polymer effect on the catalytic behavior of metal complexes attached to macromolecular ligands is found in the potentiality of yielding new species with striking catalytic properties, which arise from the formation of chemical species not predictable from knowledge based on the corresponding monomeric analogs.

The possibility of obtaining coordinatively unsaturated polymer-bound metal species has been, in fact, well established in several cases, resulting in improved catalytic behavior of heterogenized complexes.

This point also includes the formation of finely dispersed metal species, isolated atoms, and clusters within a polymer matrix. The occurrence of such effects is to be related to the very high local concentration of functional groups supplied by the macromolecular ligand, which can lead to more extensive displacement of the low molecular weight ligands present in the metal precursor. The resulting "naked" metal atoms can then be coordinatively embedded and stabilized by the polymer as isolated metal atoms or aggregates, depending on the chemical species involved.

A detailed discussion of all the examples available is at present not feasible as complete coverage of the subject systems is difficult to achieve, taking also into account recent developments with metal particles finely dispersed in polymer matrices [6]. Thus, this presentation will be limited to some arbitrarily selected examples to give a description of the established results as well as the many problems still open, with the hope of providing useful indications to orient future directions of research.

2. EFFECT OF THE POLYMER ON THE STRUCTURE OF THE METAL COMPLEX

As already mentioned, the reaction of structurally ordered macromolecular ligand with a transition metal complex results generally in the formation of a metal derivative in which metal atoms in different environments are present.

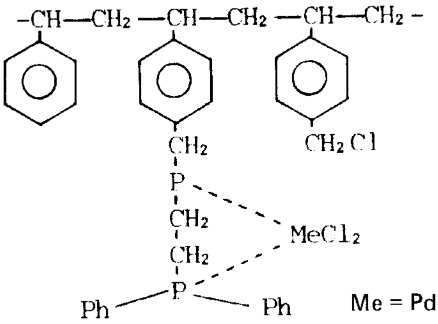
The formation of different metal-containing species has been experimentally shown by ^{31}P NMR for the binding of $[RhCl(C_2H_4)_2]_2$ to crosslinked phosphenated polystyrene [7]. Mononuclear and polynuclear species have been revealed by IR and electronic spectroscopy for the complexation of $Pd(OAc)_2$ on phosphenated polymers, the content of different species depending on the starting Pd/P ratio [8]. EXAFS analysis of complexes obtained by binding $RhBr(PPh_3)_3$ to variously crosslinked styrene-divinylbenzene phosphenated resins indicated that, with 2% crosslinking, the dinuclear structure [(Ⓟ $-PR_2)_2RhBr]_2$ largely prevails, whereas with 20% crosslinking a mononuclear structure of (Ⓟ $-PR_2)_3RhBr$ type is observed [9].

The preparative procedure also strongly affects the structure and catalytic activity of the polymer-supported metal complex as shown by binding $RhCl(PPh_3)_3$ or $RuCl_2(PPh_3)_3$ to phosphenated polymers [10].

Appropriate selection of the binding groups attached to the macromolecular chain and of metal precursor can, in some cases, lead to a uniform structural situation of the supported metal species. These typical situations are often observed when the functional groups of the polymer each have the possibility of bidentate (or multidentate) binding, as for complexes having Structure (I) obtained by ligand exchange from $PdCl_2(C_6H_5CN)_2$ or $PtCl_2(C_6H_5CN)_2$ and polystyrene functionalized by the chelating diphenylphosphine $K^+-P-(Ph)-CH_2-CH_2-PPh_2$ [11].

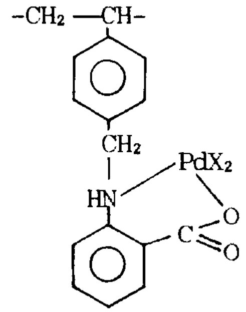
A similar situation holds for Pd complexes with Structure (II) obtained by fixing a functionalized derivative of anthranilic acid to crosslinked polystyrene [12].

The substantially identical Structure (III) for homogeneous and polymer-supported species is also proposed [13] for ethylene oligomerization cata-



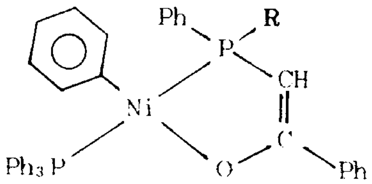
Me = Pd or Pt

(I)



(II)

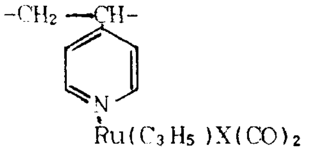
lysts based on nickel derivatives with a phosphorus-oxygen chelate ligand (benzoyl methylene phosphorane and its polymer-attached analog, respectively).



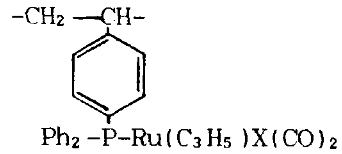
(III)

where R = –Ph for the homogeneous catalyst
R = $-C_6H_4-$Ⓟ for the polymer-supported catalyst

In addition, a uniform structure of the polymer-metal complex is possible when the reaction between ligands in the polymer and transition metal precursor takes place along a well-established stoichiometric pathway. Accordingly, the reaction between macromolecules containing electron-donating groups (tertiary N or P) and $Ru(C_3H_5)X(CO)_3$ (X = Cl or Br) occurs with displacement of only one CO molecule [14]. A Ru/N (or Ru/P) ratio close to 1 can be obtained in the polymer complex, giving rise to structures of type (IV) and (V), respectively. In the case of (V), the structure is confirmed by comparison of spectroscopic properties with the monomeric analog $Ru(C_3H_5)X(CO)_2(PPh_3)$. An analogous complex with pyridine has never been isolated due to its instability.



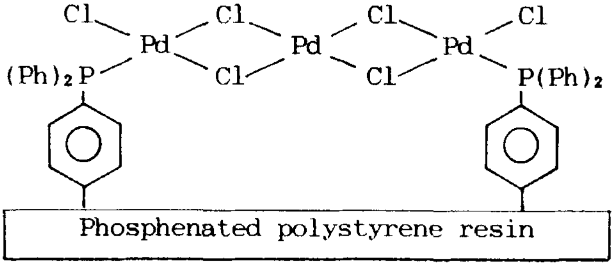
(IV)



(V)

The amount of binding groups of the macromolecular ligand accessible for the formation of a particular complex is in some way determined by the type of reaction. Taking into account this concept, an attempt was made to obtain definite Pd complexes in phosphenated polystyrene resins [15]. The metal precursor $PdCl_2L_2$ (L = pyridine (Py) or benzonitrile (PhCN)) was accordingly reacted with resins having different surface areas and phosphine contents.

Starting with $PdCl_2Py_2$, varying amounts of the complex $PdCl_2Py(P)$ (P = phosphenated polystyrene unit) are formed together with the complex $PdCl_2(P)_2$. The former monosubstituted complex exists even at formal P/Pd ratios above 2, probably due to the presence of inaccessible phosphine groups in the resin. Starting with $PdCl_2(PhCN)_2$, the polymer-bound derivatives do not contain any benzonitrile, thus suggesting an easier displacement of this ligand, probably because of its low complexation ability. In any case, these results suggest nonunique structures of the metal species in the two cases. Indeed, IR spectroscopy in the spectral range of characteristic vibra-



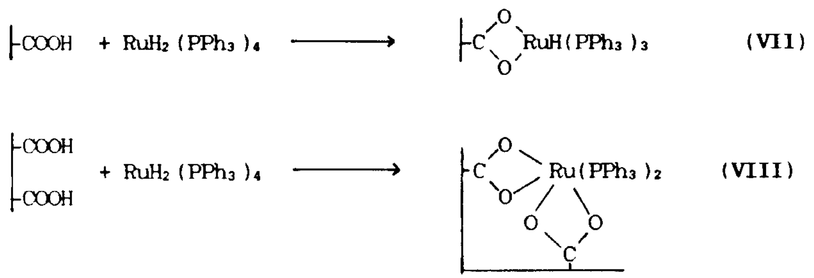
(VI)

tions of the Pd–Cl stretching band and of some additional ligands as CO and 4-cyanopyridine used as the probe also indicates the formation of $(PdCl_2)_n$ chains linked to phosphine groups (VI) which should be responsible for the easy reducibility of some of the Pd atoms in the polymeric complex.

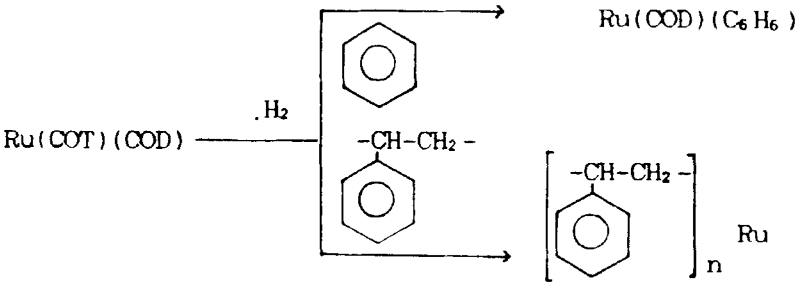
More complex situations with respect to the reaction with monomeric analogs, as well as formation of different metal-anchored species, has been observed for Ru(II) and Rh(I) hydridophosphine complexes with polymers carrying carboxylic groups [16, 17]. In particular, even taking into account only the most probable reaction pathways (Scheme 1), the formation of the mono(carboxylato) species (VII) and the bis(carboxylato) species (VIII) is predictable and experimentally demonstrated.

Formation of polymer-supported metal species completely different from those obtained when using an analogous monomeric ligand is observed when reacting Ru(COT)(COD) (COT = cycloocta-1,3,5-triene; COD = cycloocta-1,3,5-triene; COD=cycloocta-1,5-diene) with polystyrene under the same conditions used to prepare the Ru(benezene)(COD) complex [17] (scheme 2).

Indeed, for the reaction with the polymer, both COD and COT are displaced with the formation of a product containing polystyrene and Ru only. A similar complex with the general formula $[(C_6H_5)(CH_2)_3(C_6H_5)]Ru_2$ was obtained when reacting Ru(COT)(COD) with 1,3-diphenylpropane under the above conditions [18], thus supporting the proposed structure with small Ru clusters attached to benzene rings and also in agreement with EXAFS analysis [19], as schematically depicted in Fig. 1. This last shows that Ru atoms are complexed to phenyl rings and tend to group in small clusters, depending on Ru loading [20]. A formally different but substantially similar behavior has been observed for polymer-attached cyclopentadienyldicarbonyl cobalt when compared with the corresponding soluble analog $CoCp(CO)_2$ [21].



SCHEME 1.



SCHEME 2.

Although the metal environment appears the same in both systems under preparative conditions, they show pronounced differences when exposed to a CO/H_2 atmosphere at 190-200°C. The homogeneous complex decomposes under these conditions and does not show unusual catalytic properties, whereas the supported system exhibits good Fischer-Tropsch activity. The analytical investigation does not permit full identification of catalytic polymer-supported species which show reversible decarbonylation/carbonylation. The experimental data suggest that the specific chemical environment provided by the macroporous polystyrene resin in the vicinity of the metal is responsible for the formation of reactive "naked" CoCp species.

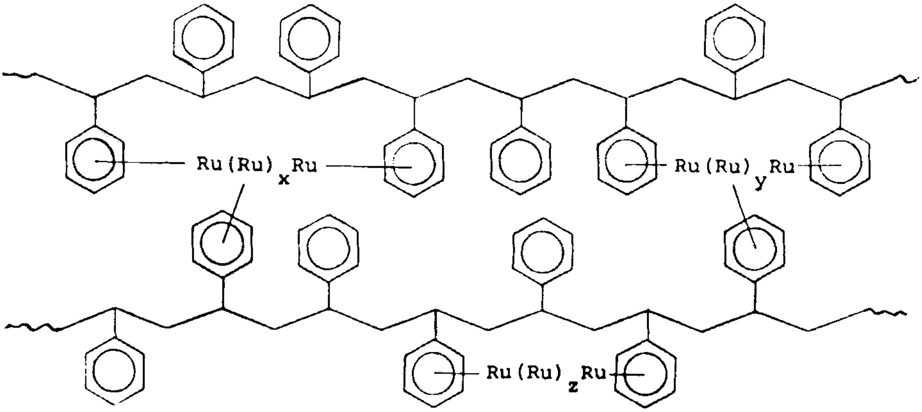


FIG. 1. Schematic representation of some possible structures of Ru clusters coordinated to polystyrene.

The complexity of reactions involving transition-metal derivatives and polymeric ligands has also been clearly demonstrated for the interaction of a series of Co subgroup clusters $Rh_xCo_{4-x}(CO)_{12}$ (x = 4,2,1,0) and $Ir_xCo_{4-x}(CO)_{12}$ (x = 4, 2, 0) with amine-functionalized polystyrene [22], different reactivity patterns existing for the different clusters with the different supports.

From this short discussion and related examples on structural and preparative aspects of polymer-supported transition-metal complexes, the evident conclusion is that, after binding, the metal is generally located in an environment substantially different from that of the corresponding monomeric analog, even if the homogeneous and heterogenized systems are coordinatively identical. Moreover, in most cases the environment is not the same for all the metal atoms. This can have profound influence on the catalytic behavior.

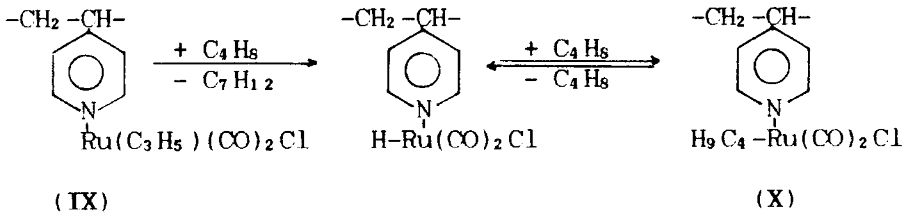
3. EFFECT OF THE POLYMER ON THE STABILITY OF THE REACTIVE SPECIES

Fixation on the polymer matrix can also render coordinatively unsaturated species long-living enough to be detected by spectroscopic methods. This has indeed been possible for hydrido- and carboxylato-triphenylphosphine rhodium complexes for which the catalytic activity increases linearly with increasing amount of coordinatively unsaturated species. These last can be measured indirectly by exposure of solid samples to O_2 with formation of ESR-active $Rh^{II}O_2$ species [24]. It is worth noting that the content of ESR-active species depends on the macromolecular ligand structure, thus suggesting the possibility of modulating the catalytic activity by modifying the structure of the polymer matrix, as discussed in the next section.

Reactive intermediates formed from polymer-supported transition-metal complexes are less prone to deactivation and decomposition reactions than homogeneous systems, thus allowing their analytical detection and practical recovery.

Probably the first example is offered by polymer-bound titanocene which on reaction with BuLi gives a more active hydrogenation catalyst than titanocene or benzyltitanocene dichloride. This result was explained on the basis of the higher concentration of "monomeric" metal species determined by ESR, thus concluding that polymer attachment prevents the coupling to inactive species of reduced titanocene complexes [25].

In the case of Complex (IX), the mechanism of isomerization is based on the formation of the alkyl derivative (X) (Scheme 3) which could never be isolated for low molecular weight ligands.



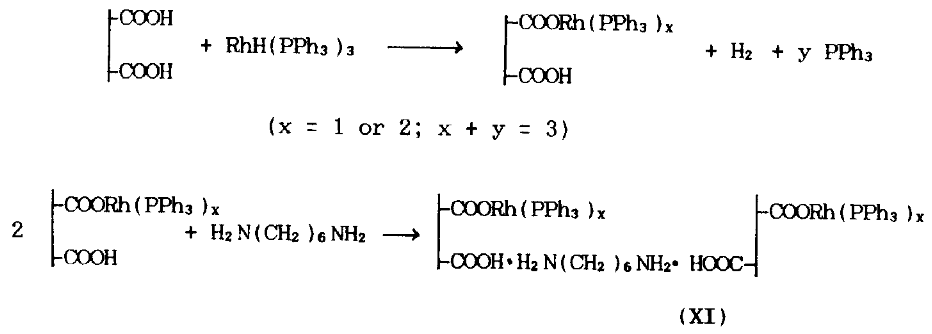
SCHEME 3.

Mass spectrometric analysis of the catalyst after removing the olefin under very high vacuum gave clear evidence of the formation of (X), as a peak at m/e 57 (C_4H_9) was present. The stability of the catalyst allowed recycling it with substantially constant catalytic activity [14].

Triphenylphosphine-polyacrylato-Rh(I) complexes (XI), prepared by reaction of $RhH(PPh_3)_3$ with atactic poly(acrylic acid) and crosslinked by addition of hexamethylenediamine (Scheme 4), showed better catalytic activity for 1-pentene hydrogenation and isomerization than homogeneous monomeric analogs [26]. These systems also show remarkable catalytic stability and very constant selectivity upon recycling.

In some cases the presence of a stoichiometric excess of binding functions in the polymer matrix can be useful for the fixation of solubilized metal species, provided that the matrix is rigid enough to avoid deactivation by polycoordination [26].

Postreaction stabilization of pristine polymer-metal complexes is reported



SCHEME 4.

also for systems obtained by starting with $RuCl_3 \cdot 3H_2O$ and a carboxylate polymer derived from a chloromethylated polystyrene resin and then adding phenylacetic acid moieties [27]. In the first step, unidentate metal acetate bonding is obtained with ready metal leaching under catalytic conditions (DMF at 85°C). This can be avoided by addition of sodium acetate to the pristine polymer complex, resulting in the formation of bridging acetate groups and suggesting that the Ru complex is the polymer-supported analog of $[Ru_3O(O_2CMe)_6(H_2O)_3]^+$. This stabilized catalyst is not sensitive to O_2 and can be recycled with only a slight activity decrease.

The possibility of identifying reaction intermediates stabilized by polymeric supports has been recently shown, even if one starts with transition metal clusters. Thus the anionic cluster $[HFe_3(CO)_{11}]^-$ was attached to commercial anion-exchange resin beads or poly(styrene-divinylbenzene) membranes functionalized with quaternary ammonium groups. The system is capable of the stoichiometric reduction of nitrobenzene to aniline. The change of the IR spectrum of the complex by the interaction of the substrate nitrobenzene has been associated with the formation of the intermediate (XII), as identified by comparison with the synthetic analog $[HFe_3(CO)_9NPh]^-(HNEt_3)^+$ [28].

$$\text{Ⓟ}-CH_2\overset{+}{N}Et_3\ [HFe_3(CO)_9NPh]^-. \qquad \text{(XII)}$$

In conclusion, fixation of homogeneous metal catalysts to polymeric supports can be regarded as a way of approaching mechanistic studies as well as of improving their stability and recycling.

4. EFFECT OF THE POLYMER ON CATALYTIC PROPERTIES

The two preceding sections have shown the real difficulty of obtaining polymer-supported complexes with an unique, well-defined structure. This is certainly due to the complexity and very specific nature of the macromolecular ligand. Moreover, even the most powerful analytical techniques are sometimes not very helpful for obtaining unequivocal answers at the molecular level. An accurate examination of the literature would probably bring us to the in some ways paradoxical conclusion that the catalytic behavior may give more information about the nature of the active species than a static structural analysis.

This is certainly valid when suitable homogeneous analogs are available and their catalytic properties and reaction mechanisms have been exhaustively investigated. Indeed, when the nature of the active species attached to the polymer ligand is in some way clarified, these polymer-supported catalysts are really hybrid systems, part way between purely homogeneous and heterogeneous catalysts.

However, when the structure of the metal complex in the macromolecular matrix is difficult to identify or has no homogeneous analog and, in addition, the polymer is capable of appreciably affecting the reaction, the system must be regarded as a new catalyst. From this point of view, this approach opens the door to a new, only partially investigated area in metal catalysis.

In an attempt to describe some of the above concepts, a few examples will be reported, organized in two groups depending on structural relationships with potential monomeric analogs acting as homogeneous catalysts.

4.1. Same Structure as the Monomeric Analog

In case the structure of the polymer-metal complex is well defined and resembles that of a monomeric analog, a lower catalytic activity can be, in general, expected because of the heterogeneous character, which reduces the number of active centers available to the substrate. Moreover, steric effects become more important, providing an additional decrease in the reaction rate, particularly with bulky reagents. The observation has been made on several occasions, and a very typical example is offered by $Ru(C_3H_5)X(CO)_2(PPDPS)$, where PPDPS indicates a phosphenated unit of linear polystyrene samples with different molecular weights and tacticity. The complexes thus obtained were used for the isomerization of 1-butene to a mixture of Z- and E-2-butene in a liquid medium (toluene) capable of dissolving the monomeric complex with triphenylphosphine, but only able to swell the various polymeric catalysts. It was observed that the reaction rate decreased for various phosphenated ligands in the order [14] PPh_3 > low molecular weight atactic PPDPS > high molecular weight atactic PPDPS > high molecular weight isotactic PPDPS (where PPDPS = poly-*p*-diphenylphosphinostyrene).

Such results clearly indicate that the better swelling of the polymeric ligand by the liquid reaction medium increases the portion of available reaction sites, thus helping the polymer-attached catalyst to approach the activity of the homogeneous system where all Ru atoms act as catalytic sites.

The above situation is, of course, observed when the specific polymer ligand/metal complex reaction gives the same metal environment as the monomeric system, with the polymer acting as a chemically inert support. Indeed, other factors due to the macromolecular structure can be involved, and the catalytic process is consequently subject to several polymer effects.

Apart of the actual metal complex structure, additional physical effects arise from the dependence of chain mobility of the polymer support on temperature [29]. This has been observed for a rhodium complex anchored on three types of phosphenated polystyrene which were crosslinked with divinylbenzene or ethylene dimethacrylate. DSC glass transitions were separately observed for the flexible polymer supports and their polymer-anchored rhodium complex catalysts. Discontinuous drops in the Arrhenius plot of the ethylene hydrogenation activity were observed for these flexible polymer catalysts, whereas for the rhodium complex anchored to a highly crosslinked rigid polymer, neither a glass transition nor such a discontinuity in the catalytic activity could be detected. This reversible activity drop is discussed in terms of changes in the stability and the coordination state of the ethylene complex influenced by the micro-Brownian motions of the polymer network.

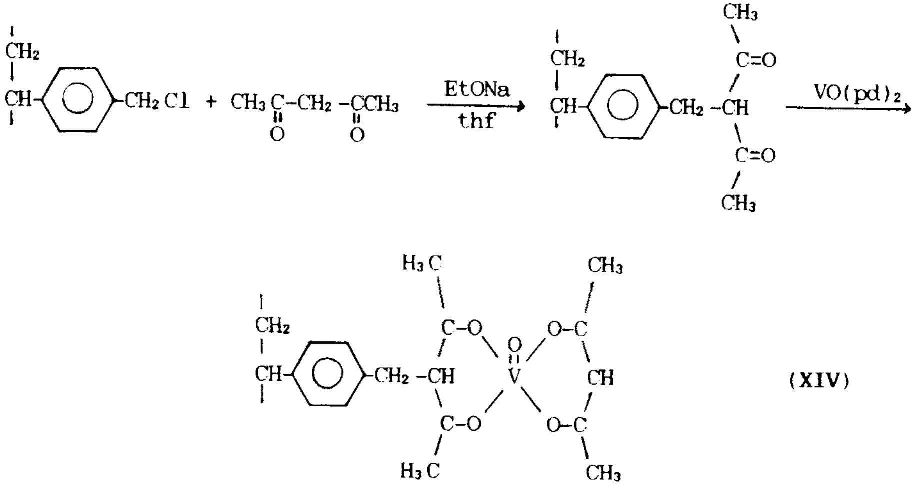
A substantial confirmation of the "negative" physical effect of the resin on catalytic activity has also been observed in the butene isomerization by triosmium clusters anchored to resins carrying primary alcohol groups [30]. The structure of coordinated metal species (XIII) (Scheme 5) was shown by IR analysis to be substantially identical to the corresponding monomeric analog, this last being, however, much more active.

Indeed, it is reasonable to discuss here some other examples in which, *even if the identity of structure is not fully proved, the general characteristics* suggest that the use of a polymeric ligand does not dramatically affect the metal environment. As far as catalysis is concerned, this does not necessarily mean the same behavior for soluble homogeneous and supported systems. In addition to the already mentioned macroscopic effects connected with the physical behavior of the support, other effects may arise at the molecular level, particularly when the polymer contains functional groups not involved in the metal binding and capable of exerting a synergistic effect in the catalytic process.

This can be achieved, for example, by specific interactions with the substrate providing a high local concentration of reagents or by controlling deactivation. In this connection, some examples still deserve consideration from the point of view of the present paper even if it is not possible to discriminate unequivocally between the polymer effects exerted at the level either of structure determination or of catalytic behavior.

$$Os_3(CO)_{12} + \textcircled{P}-CH_2CH_2OH \rightarrow HOs_3(CO)_{10}-O(CH_2)_2-\textcircled{P} \quad \text{(XIII)}$$

SCHEME 5.



(XIV)

SCHEME 6.

These aspects were well discussed more than 10 years ago by performing a detailed structural and kinetic comparison between phosphenated polystyrene Rh, Ru, and Fe complexes and their homogeneous analogs [31].

Thus, synergistic action of the polymer ligand in the decomposition of *t*-butyl hydroperoxide has been shown for polymer-supported oxobis(pentane-2,4-dionato)vanadium(IV) catalysts (XIV) [32]. These systems, prepared according to Scheme 6, catalyze, respectively, the oxidation of Me_2SO, Bu_2S, and cyclohexane in the presence of *t*-BuOOH.

Indeed, the anchored species give better yields than the homogeneous analogs thanks to the lower deactivation rate which overwhelms the lower activity.

By supporting molybdenum(V)dithio-carbamato derivatives $Mo_2O_3(S_2CNEt_2)_4$ on the same crosslinked polystyrene, a catalyst giving the same oxidation reactions as above was obtained [33]. Again, better yields are achieved than with the monomeric analogs because the dithiocarbamate ligand gives a side reaction that consumes the oxidizing agent but is sterically hindered by the polymer.

Three kinds of supported catalysts have been prepared by reacting $Ru(O_2CCF_3)(CO)(PPh_3)_2$ with polystyrene-divinylbenzene resins containing diphenylphosphine, carboxylic, or both functional groups, respectively [34]. The IR analysis of characteristic vibrational bands of carboxylate and carbonyl groups indicated a structure of the ruthenium complex after fixation similar to that of the starting complex. These systems have been used as catalysts for the dehydrogenation reaction of alcohols, which is known to be activated by the presence of free carboxylic acids [35]. The resin-attached complexes show, in general, a reduction of activity when compared with the homogeneous catalyst, as expected by considering diffusion limitations. In addition, effects of the structure of the polymeric ligand are also observed, the phosphine-containing supports giving higher activity than those containing only carboxylic groups.

The sulfur-containing macromolecular ligands seem to produce transition metal complexes with higher stability and activity than the corresponding phosphine-polymer derivatives. The maintainence of catalytic activity after reduction of activated alkenes with iodobenzene to give phenyl-substituted derivatives has been attributed to the presence of –SH groups that prevent Pd(0) and Pd(II) species from aggregation [36].

The attachment of $-CpRhL_2$ moieties to a polystyrene resin results in the first heterogeneous catalyst for the synthesis of pyridines by cyclization of alkynes and nitriles. However, selectivity and activity of these systems are lower than those for the homogeneous process in the presence of $Rh(\eta^5\text{-}C_5H_5)L_2$ catalyst [37]. Moreover, the supported catalyst shows poor durability due to both rhodium leaching and rearrangement during the catalytic cycle. These results indicate that the simple attachment to a polymer is not a universal way of converting a homogeneous catalyst into an easy recoverable heterogeneous system with similar application properties.

A significant example in the same direction is given by the observed behavior of ruthenium(II) complexes supported on polycarboxylate matrices and used as catalysts for the hydrogenation of aldehydes with alcohols as the hydrogen source. In this case the excess of free carboxylic groups present in heterogeneous systems obtained by reacting $RuH_2(PPh_3)_4$ with preformed carboxylic acid resins or atactic poly(acrylic acid) promotes side reactions involving the aldehyde substrate. This drawback can be only partially overcome by increasing the metal loading of the heterogeneous catalysts [38]. Catalytic activities and selectivities comparable to those of analogous carboxylate ruthenium complexes can be achieved only by following a completely different route for the preparation of metal-polymer systems, based on the co- or terpolymerization of bis(acrylato)bis (triphenylphosphine)Ru(II) monomers with methyl methacrylate and 1,4-butanediol dimethacrylate.

4.2. Structure Different from Monomeric Analogs

More dramatic effects and improved catalytic behavior can be observed in many cases when formation of coordinatively unsaturated species, particular steric effects, stabilization of reaction intermediates, and formation of unexpected metal environments can give rise to higher reactivity, different selectivity, longer life, and new catalytic reactions.

The occurrence of coordinatively unsaturated metal species was proposed in 1972 to explain the higher activity observed in some cases for transition-metal complexes attached to phosphenated polystyrene resins [23]. Similar explanations have been put forward for complexes obtained from $RuH_2(CO)(PPh_3)_3$ and polymers with carboxylic groups (XV) [17] (Scheme 7). Indeed, these complexes show increasing catalytic activity by decreasing the P:Ru ratio to below 2, which is expected on the basis of the stoichiometry of monomeric models.

By reacting Ru(COT)(COD) under hydrogen with the polymer of an aromatic vinyl monomer, such as styrene or 1-vinylnaphthalene, it has been shown that the reaction of a transition-metal complex bearing easily displaced low molecular weight ligands, with the ligand containing at least two aromatic rings in the proper relative positions, can provide finely dispersed metal particles or small clusters complexed to the polymer matrix [39], thus stabilizing the substantially "naked" metal [40].

Also, the dependence of the catalytic properties on the nature of the aromatic polymer ligand, metal loading, and substrate, as well as the reaction stereochemistry, can be better explained by taking into account substrate activation by coordination and steric effects at the molecular level, as observed for homogeneous Ru and Rh complexes active for arene hydrogenation. It is of interest to note that these polystyrene- or poly-1-vinylnaphtalene-supported ruthenium clusters show extraordinary catalytic activity in hydrogenating aromatic and other functional groups ($-C{=}O$, $-NO_2$, $-CN$, . . .) in addition to the olefinic double bond, which is the only active substrate for the corresponding homogeneous catalyst $Ru(C_6H_6)(COD)$ [18, 39]. Moreover, the metal species remain bonded to the aromatic polymer during the entire reaction time, and no loss of activity is observed on reuse. This stability is connected to the lack of hydrogenation of the aromatic side chains of the macromolecular ligand. Indeed, even linear polystyrene is not hydrogenated under the reaction conditions, thus indicating the substantially heterogeneous character of the catalyst [41].

$$\textcircled{P}-COOH + RuH_2(CO)(PPh_3)_3 \longrightarrow \textcircled{P}-COORuH(CO)(PPh_3)_x$$

$$x \leqslant 2 \qquad\qquad \text{(XV)}$$

SCHEME 7.

The possible occurrence of strong coordinate interactions between metal particles and the polymeric support has suggested interesting ways for preparing this novel class of heterogenized transition-metal catalysts.

The use of polymeric supports containing ligands capable of stabilizing zero-valent species in order to avoid migration of the metal centers to form crystallites seems to be the proper way to approach the problem. This has been experimentally confirmed by employing the well-known styrene-divinylbenzene copolymers functionalized with diphenylphosphine groups and reducing $[RhCl(COD)]_2$ supported on it in a stream of hydrogen at 130°C [42]. X-ray scattering techniques have demonstrated that the metal particle size and dispersion are determined mainly by the amount of phosphine groups, thus suggesting strong metal-ligand interaction. ESR investigation has confirmed this picture, showing that, whereas magnetically diluted Rh(0) centers are present at high P/Rh ratios, metal crystallites play a dominant role at low P/Rh ratios, as shown by the broad unresolved signals [43].

Similar concepts can be used to describe the structure and to interpret the catalytic properties of Pt and Pt-Sn hydrogenation catalysts supported on polyamides (nylon 66 and 610) [44]. Some differences in catalytic activity and selectivity toward different substrates between the catalyst obtained by hydrogen reduction of H_2PtCl_6 absorbed on nylon and Pt on carbon suggest the existence of interactions of Pt with support [45].

A further application of polymeric supports to stabilize fine metal particles is offered by the possibility of preparing colloidal dispersions of various metals by reduction of the corresponding metal salts in the presence of protective polymers [46]. Average diameters of the metal particles in the range 9-150 Å can be obtained in this way. In the case of dispersed colloidal rhodium prepared by reduction with CH_3OH of $RhCl_3$ adsorbed on poly(vinyl alcohol) or poly-(*N*-vinyl-2-pyrrolidone), particles with 9 Å average diameter have high catalytic activity for hydrogenation of internal olefins. The colloidal palladium catalyst with particles of 18 Å average diameter exhibits high catalytic selectivity for hydrogenation of dienes to monoenes.

The protective polymer plays an important role in stabilizing the colloidal dispersion and in increasing the catalytic selectivity through interaction with the metal particles. Aluminum copper chloride protected by crosslinked polystyrene is also a solid adsorbent of carbon monoxide. The polymer protects the water-sensitive metal species against moisture contained in the gas. The protecting effect of the polymer depends on the nature of the solvent used in the preparation of the solid adsorbent. However, the structure of the final catalyst is also polymer-dependent because the metal ions must be coordinated on it before reduction.

5. FINAL REMARKS

After more than 15 years of continuous, even if sometime irregular, research activity on the preparation and catalytic use of transition metal/polymer complexes, the area appears still only partially exploited, with many questions remaining unanswered. In the preceding pages the topic has been covered in the only presently possible way by arbitrarily selecting some, in our opinion, illuminating examples. As a consequence, these final remarks are not of really general significance, but probably reflect the actual situation better than an only apparently successful integrated and comprehensive review.

The basic points evidenced throughout this paper reflect an attempt to separate the major polymer effects that have been identified for preparation, structure, stability, and catalytic activity.

As far as preparation and structure are concerned, it has been clearly shown that in most cases the multidentate character of macromolecular ligands hinders the preparation of species with uniform structure, unless the reaction between the metal precursor and the binding groups is highly controlled and specific. This last can be, in general, improved by attaching to the macromolecular matrix a bi- (or tri-) dentate low molecular weight ligand which clathrates the metal and prevents it from reacting with other groups along the chain. In any case, really well-defined structures are the exception rather than the rule, and it is not very profitable to pursue this as the main objective.

Indeed, the main purpose of this paper is to stress once again the great potential of polymer-supported transition metals as catalysts, after having pointed out the types of structure one can expect at the molecular level.

Macromolecules are very sensitive to the molecular environment, and their properties, both of the ligand and the catalyst components, can be physically modulated by changing, for instance, the temperature and the reaction medium. Moreover, the binding properties of a given group can be changed by changing the concentration along the chain, the distance from the backbone, and the nature of the adjacent units in copolymer structures. In crosslinked resins, molecular rigidity of the support and porosity can be controlled by varying the degree of crosslinking. Moreover, the high local concentration of binding groups can drive the complexing reaction into completely new directions, thereby ending up with unexpected structures. These last can also consist of reactive intermediates that become long living due to entrapment in the more or less rigid cage provided by the polymeric support.

This appealing complexity with its practically unlimited possibilities for designing hybrids between homogeneous and heterogeneous catalysts is also responsible for the limited applicability of these systems. Indeed, the difficulty of obtaining sites of uniform structure, the versatility and mobility of the macromolecule, the temperature sensitivity typical of the organic molecules, the structural rearrangements during the catalytic process, and even the catalytic activity by groups in the polymer makes them suspect for industrial processes.

Certainly many problems could be overcome if these new systems would display activity under very mild reaction conditions, as metal enzymes do. Certainly polymer-metal systems could acquire more prestige if they could be used for specific reactions not easily carried out with conventional systems.

The idea of using polymers for converting homogeneous catalysts into heterogeneous ones without losing all good properties certainly suffers from oversimplification. Attempts to use catalysts belonging to this class only in catalytic reactions typical of petrochemistry are certainly useful for an understanding of their basic properties, but lack originality and creativity. New areas and new structures can be made available by using this powerful technique. New directions in metal catalysis [47] are offered by polymer-supported (or embedded) clusters and metal particles. New exciting development may be finally predicted by looking to the sophisticated behavior of metal enzymes [48], which should be considered when designing new structures and discovering new applications.

REFERENCES

[1] C. U. Pittman Jr., in *Comprehensive Organometallic Chemistry,* Vol. 8 (G. Wilkinson, F. G. A. Stone, and G. Abel, eds.), Oxford, 1982, p. 533.

[2] F. Ciardelli, G. Braca, C. Carlini, G. Sbrana, and G. Valentini, *J. Mol. Catal., 14,* 1 (1982).

[3] E. Tsuchida, *Macromol. Rev., 16,* 397 (1982).

[4] H. Pracejus, East German Patent 92,031.

[5] A. Kinting, C. Döbler, H-J. Kreuzfeld, and H. Krause, *Wiss. Z. Karl-Marx-Univ. Leipzig, Math.-Naturwiss. R., 34,* 169 (1985) and references therein.

[6] J. S. Bradley, E. Hill, M. E. Lenowicz, and H. Witzke, *J. Mol. Catal., 41,* 59 (1987).

[7] A. J. Naatgeboren, R. J. Nolte, and W. Drenth, *J. Am. Chem. Soc., 102,* 3350 (1980).

[8] V. A. Semikolenov, V. A. Likholobov, G. Valentini, G. Braca, and F. Ciardelli, *React. Kinet. Catal. Lett., 15,* 383 (1980).

[9] J. Reed, P. Eisemberg, B. K. Teo, and B. M. Kincaid, *J. Am. Chem. Soc., 100,* 2375 (1978).

[10] S. Torroni, G. Innorta, A. Foffani, F. Scagnolari, and A. Modelli, *J. Mol. Catal.*, *33*, 37 (1985).
[11] H. J. Kreuzfeld, *Z. Chem.*, *18*, 231 (1978).
[12] N. L. Holy and R. S. Shelton, *Tetrahedron*, *37*, 25 (1981).
[13] M. Penchert and W. Keim, *J. Mol. Catal.*, *22*, 289 (1984).
[14] C. Carlini, G. Braca, F. Ciardelli, and G. Sbrana, *Ibid.*, *2*, 379(1972).
[15] C. Andersson and R. Larsson, *J. Catal.*, *81*, 179, 194 (1983).
[16] G. Braca, F. Ciardelli, G. Sbrana, and G. Valentini, *Chim. Ind.* (*Milan*), *59*, 766 (1977).
[17] G. Valentini, G. Sbrana, and G. Braca, *J. Mol. Catal.*, *11*, 383 (1981).
[18] P. Pertici, G. Vitulli, C. Carlini, and F. Ciardelli, *Ibid.*, *11*, 353 (1981).
[19] A. Bianconi, M. Dell'Amico, A. Giovannelli, E. Burattini, N. Cavallo, P. Patteri, E. Pancini, C. Carlini, F. Ciardelli, D. Papeschi, P. Pertici, G. Vitulli, G. Dalba, P. Fornasini, S. Mobilio, and L. Palladino, *Chem. Phys. Lett.*, *90*, 257 (1982).
[20] G. Dalba, P. Fornasini, F. Rocca, P. Pertici, and E. Burattini, *J. Phys. C8*, 331 (1986).
[21] P. Perkins and K. C. Vollhardt, *J. Am. Chem. Soc.*, *101*, 3985 (1979).
[22] R. A. Dubois, P. E. Garron, G. E. Hartwell, and D. L. Hunter, *Organometallics*, *3*, 95 (1984).
[23] J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Am. Chem. Soc.*, *94*, 1789 (1972).
[24] G. Braca, G. Sbrana, G. Valentini, A. Colligiani, and C. Pinzino, *J. Mol. Catal.*, *7*, 457 (1980).
[25] R. H. Grubbs, C. Gibbon, L. C. Kroll, W. D. Bonds Jr., and C. H. Brubaker Jr., *J. Am. Chem. Soc.*, *95*, 2373 (1973).
[26] G. Valentini, G. Sbrana, G. Braca, and P. Da Prato, *J. Catal.*, *32*, 291 (1985).
[27] C. P. Nicolaides and N. J. Coville, *J. Mol. Catal.*, *24*, 375 (1984).
[28] J-B. NGuini Effa, B. Djebailli, J. Lieto, and J. P. Aune, *J. Chem. Soc., Chem. Commun.*, p. 408 (1983).
[29] T. Uematzu, Y. Nakazawa, F. Akutsu, S. Shimazu, and M. Miura, *Makromol. Chem.*, *188*, 1085 (1987).
[30] J. Lieto, M. Prochazka, D. B. Arnold, and B. C. Gates, *J. Mol. Catal.*, *31*, 89 (1985).
[31] G. Strathdee and R. Given, *Can. J. Chem.*, *52*, 3000 (1974).
[32] S. Bhaduri, A. Ghosh, and H. Khwaja, *J. Chem. Soc., Dalton Trans.*, p. 447 (1981).
[33] S. Bhaduri and H. Khwaja, *Ibid.*, p. 415 (1983).
[34] W. K. Rybak and J. J. Ziolkowski, *J. Mol. Catal.*, *11*, 365 (1981).

[35] A. Dobson and S. D. Robinson, *Inorg. Chem.*, *16,* 1321 (1977).
[36] X. Li, H. Liu, and Y. Jiang, *J. Mol. Catal.*, *39,* 55 (1987).
[37] P. Diversi, G. Ingrosso, A. Lucherini, and A. Minutillo, *Ibid.*, *40,* 359 (1987).
[38] G. Valentini, A. Cecchi, C. Di Bugno, G. Braca, and G. Sbrana, in *Homogeneous and Heterogeneous Catalysis* (Yu. Yermakov and V. Likholobov, eds.), VNU Science Press, Utrecht, The Netherlands, 1986, p. 765.
[39] F. Ciardelli and P. Pertici, *Z. Naturforsch.*, *40b,* 133 (1985).
[40] G. Wilke, *Angew. Chem., Int. Ed. Engl.*, *2,* 105 (1963).
[41] J. P. Collman, K. M. Kosydar, M. Bressan, W. Lamanna, and T. Garrett, *J. Am. Chem. Soc.*, *106,* 2569 (1984).
[42] G. Cocco, S. Enzo, F. Pinna, and G. Strukul, *J. Catal.*, *82,* 160 (1983).
[43] T. Beringhelli, A. Gervasini, F. Morazzoni, F. Pinna, and G. Strukul, *Ibid.*, *88,* 313 (1984).
[44] S. Galvagno, P. Staiti, and P. Antoniucci, *J. Chem. Soc., Faraday Trans. I*, *79,* 2605 (1983).
[45] Z. Poltarzewski, S. Galvagno, R. Pietropaolo, and P. Staiti, *J. Catal.*, *102,* 190 (1986).
[46] H. Hirai, *Makromol. Chem., Suppl. 14,* 55 (1985).
[47] M. Boudart, *J. Mol. Catal., Rev. Issue,* p. 29 (1986).
[48] R. J. P. Williams, *Ibid.*, p. 1 (1986).

Note Added in Proof. Support by the Ministry of Education (MPI-60%) is gratefully acknowledged.