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Postcrosslinking of Rhodium Catalysts Bound to Polyacrylic Acid: A Useful Technique to Enhance and Preserve Catalytic Activity

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A significant improvement of the catalytic performance of triphenylphosphine polyacrylate Rh(I) complexes, prepared by reaction of $RhH(PPh_3)_4$ with atactic polyacrylic acid, has been attained by optimizing the preparative procedure (proper choice of reagent ratio and reaction medium) and by adding a crosslinking agent (hexamethylenediamine). The crosslinked systems, insoluble in the organic solvents, have been obtained in high yields and showed a catalytic activity for pent-1-ene hydrogenation and isomerization higher than that of a low-molecular-weight analog working in solution. These systems also show a remarkable catalytic stability and a very constant selectivity upon recycle. IR spectra of the catalysts and their carbonyl derivatives, obtained upon treatment in the solid state with CO, gave information about the nature of the different metal species present within the polymeric systems and explain the different catalytic behavior of the catalysts. © 1985 Academic Press, Inc.

INTRODUCTION

Heterogenized catalysts can be prepared by means of a variety of procedures (*1*, *2*) but, analogously to heterogeneous systems, it has so far been impossible to draw general rules or operative strategies to be followed in order to obtain systems with predetermined catalytic properties. Furthermore, with respect to the chemistry of organometallic complexes with low-molecular-weight ligands, the preparation of polymer-bound catalysts through the reaction of a metal precursor with a functionalized polymer is associated with additional problems arising from the polymeric nature of the ligand (*1–4*).

It is generally very difficult to obtain systems with a predetermined ratio between metal units and binding groups due to the incomplete accessibility of all the polymer functionalities acting as potential ligands. For insoluble polymers the accessibility strongly depends on the swelling of the system in the reaction solvent. Moreover, soluble or insoluble polymeric ligands change their properties during the sequential reactions with the metal precursor. This implies that the molecules of the organometallic complex successively approaching the polymer do not find the same electronic and/or steric situation, so that the formation of metal units all in the same coordinative situation is very unlikely. In addition, the functional groups of the polymer, generally in excess with respect to the coordinated metal species, can give rise to rearrangements and deactivation of the polymer-bound species. These features account for the difficulties experienced in obtaining (and characterizing) polymer-bound catalysts with a good catalytic properties in terms of activity and durability.

The importance of the above factors in the chemistry of polymer-bound catalysts has sometimes been cited (*3*, *5*), but very few efforts have been devoted up to now to their understanding. In previous work we were able, in some favorable cases, to prepare "coordinatively unsaturated" ruthenium catalysts bound to polycarboxylate matrices showing higher catalytic activity than low-molecular-weight models (*6*, *7*). These systems, however, did not preserve

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their activity on prolonged reuse, due chiefly to deactivation of the metal sites by interactions with the free carboxylic groups of the support. Only as a result of starting with sodium salts of polymeric acids and suitable metal precursors, were long-lasting catalysts obtained, but catalytic activities were generally unsatisfactory (*8*).

The aim of the present work was to find a suitable procedure for the preparation of highly active rhodium catalysts bound to polycarboxylate matrices, and remedies for preserving the catalytic activity upon prolonged use of the systems.

EXPERIMENTAL

Materials, Equipment, and Analysis

$RhH(PPh_3)_4$ (*9*), $Rh(OCOCHMe_2)(PPh_3)_3$ (*10*), and atactic polyacrylic acid (*11*) ($\bar{M}_w = 10^6$) were prepared according to literature methods. Hexamethylenediamine (HMD) 98%, 4,4′-methylenedianiline (MDA) (Aldrich-Europe products), and pent-1-ene (Fluka product) were used without any previous treatment.

Reagents and solvents were purified according to standard procedures. IR spectra were recorded with a Perkin–Elmer 283B spectrophotometer equipped with a 3600 data station. X-Ray fluorescence (*12*) was used for the determination of phosphorus and rhodium contents in the complexes and solutions recovered after catalytic runs.

Analytical data of the catalysts are reported in Tables 1 and 2. On the basis of analytical data for Rh, P, and eventually N, the COO/Rh molar ratios in heterogenized complexes were calculated by means of the formula

$$\mathrm{COO/Rh} = [100 - (\mathrm{Rh}, \%) - 8.46 \cdot (\mathrm{P}, \%) - A \cdot (\mathrm{N}, \%)]\ 1.449/(\mathrm{Rh}, \%),$$

where 8.46 is the mol. wt. of PPh_3/ at. wt. of P; A is the mol. wt. of the crosslinking agent/2 at. wt. of N, $A = 0$ for noncrosslinked systems, $A = 4.147$ for systems obtained with HMD; and 1.449 is the at. wt. of Rh/mol. wt. of the monomeric unit of PAA minus a hydrogen atom.

The yields with respect to polyacrylic acid were calculated as

$$\mathrm{PAA\ (Yield, \%)} = [100 - (\mathrm{Rh}, \%) - 8.46 \cdot (\mathrm{P}, \%) - A \cdot (\mathrm{N}, \%)] \cdot (\text{grams of complex/grams of PAA charged}) \cdot 100$$

and those with respect to rhodium as

$$\mathrm{Rh(Yield, \%)} = (\mathrm{Rh}, \%) \cdot (\text{grams of complex/at. wt. of Rh})/(\text{g atoms of Rh initially charged}).$$

TABLE 1

Analytical Data of Heterogenized Complexes Prepared from $RhH(PPh_3)_4$ and Atactic Polyacrylic Acid (PAA) at Different COO/Rh Molar Ratios[a]

Sample[b]	mg	Starting COO/Rh	Solvent	Elemental analysis				Yields[c]	
				P, %	Rh, %	COO/Rh[c]	P/Rh[c]	Rh	PAA
BP-20-SE	98	20	Benzene/2-propanol	2.34	2.46	45.1	3.0	9	20.5
BP-10-HI	103	10	Benzene/2-propanol	4.08	8.81	9.1	1.5	17 }66.7	15.8 }93.1
BP-10-RTI	495	10	Benzene/2-propanol	4.36	5.37	15.3	2.7	49.7	77.3
BP-4-HI	490	4	Benzene/2-propanol	5.62	6.78	9.6	2.7	19.7 }26.2	60.4 }76.8
BP-4-RTI	110	4	Benzene/2-propanol	4.42	7.94	9.8	1.9	6.5	16.4
B-20-SE	41	20	Benzene	6.05	12.39	3.2	1.6	19.8	4.0
BT-20-HI	400	20	Benzene/THF	0.52	4.17	31.1	0.4	64.1	98.8
T-20-SE	202	20	THF	0.44	4.40	29.8	0.3	33.5	49.6

[a] See Experimental for reaction conditions.

[b] Abbreviations used: B = benzene; P = propanol; T = tetrahydrofuran; -20, -10, and -4 refer to the COO/Rh molar ratios used in the reaction; SE = product recovered by solvent evaporation; HI = product insoluble in the hot solution; RTI = product insoluble at room temperature.

[c] Evaluated as reported under Experimental,

TABLE 2

Analytical Data of Heterogenized Complexes Obtained by Addition of Hexamethylenediamine (HMD) as Crosslinking Agent[a]

Sample[b]	mg	Starting COO/Rh	Solvent	Elemental analysis						Yields[c]	
				P, %	N, %	Rh, %	COO/Rh[c]	P/Rh[c]	COO/N[c]	Rh	PAA
BP-20-HMD	420	20	Benzene/2-propanol	1.33	1.38	3.03	37.7	1.46	11.4	47.6	90.8
BP-10-HMD	497	10	Benzene/2-propanol	2.71	0.85	5.60	17.6	1.60	15.7	52.0	91.2
BP-4-HMD	602	4	Benzene/2-propanol	4.79	1.16	7.02	9.8	2.26	8.0	31.6	77.5
T-20-HMD	390	20	THF	0.44	1.44	3.10	40.1	0.47	11.9	45.2	91.9
B-20-HMD	304	20	Benzene	0.32	0.30	5.98	21.8	0.17	59.2	67.9	74.0

[a] See Experimental for reaction conditions; in every case the starting COO/HMD molar ratio was 20 (theoretical COO/N = 10).

[b] See footnote b of Table 1 for definitions.

[c] Evaluated as reported under Experimental.

The COO/N ratio of the crosslinked catalysts was calculated as

$$\mathrm{COO/N} = (\mathrm{Rh}, \%) \cdot \mathrm{B} \cdot 0.136/(\mathrm{N}, \%),$$

where B is the COO/Rh ratio calculated as above and 0.136 is the ratio between the atomic weights of N and P.

Preparation of the Heterogenized Catalysts

In the reactions carried out in the homogeneous system, polyacrylic acid was allowed to dissolve under argon in the refluxing solvent (2-propanol or THF) for almost 12 h and then the dropwise addition of the metal precursor solution (benzene or THF) was begun. The addition took about 4 h. When only benzene was used as reaction medium, the suspension of PAA was refluxed for 8 h in order to achieve as high a swelling as possible. The amounts used were: PAA, 370 mg (5.2 meq) dissolved in 320 ml of 2-propanol or 100 ml of THF or suspended in 60 ml of benzene; $RhH(PPh_3)_4$, 300 mg (0.26 mg at. Rh) or more, in order to obtain the desired COO/Rh ratio, dissolved in 80 ml of benzene or THF (reaction time: 30 h).

When required, hexamethylenediamine (30.2 mg, 0.52 meq) was added to the reaction mixture dissolved in 5 ml of solvent (benzene or THF).

Solid products spontaneously separated from the reaction mixture were recovered by siphoning off the hot solution (–HI samples) and the decanted solution was cooled at room temperature (–RTI samples), washed separately by decantation with the solvents used in the preparation and dried under vacuum. Otherwise, when the reaction mixture was perfectly clear at the end of the reaction time, the solution was evaporated to dryness at 40°C and the solid residue (–SE samples) was washed and dried as above.

Hydrogenation and Isomerization Experiments

Hydroisomerization reactions were carried out in a gas-volumetric apparatus as previously reported (*13*) using pent-1-ene as reactant (olefin/Rh molar ratio = 300) and 2-propanol as reaction medium. The decourse of the reaction was monitored by GLC analysis of the C_5 mixture; apparatus and analysis conditions were as previously reported (*13*).

The catalytic activity of the systems was evaluated as the time (h^{-1}) necessary to perform 150 cycles/atom (TN_{150}), corresponding to the 50% conversion of the initially charged olefin.

Solid catalysts were recovered at the end of each catalytic cycle by siphoning off the decanted solution followed by drying under a stream of H_2. The recycle of the homogeneous catalyst $Rh(OCOCHMe_2)(PPh_3)_3$ was performed by stripping off the solvent and reaction products using a H_2 stream at room temperature.

RESULTS AND DISCUSSION

Homo- and copolymers of acrylic acid in aqueous or alcoholic medium have been described in the literature for the preparation of metal salts (*14–19*), used as homogeneous (*18*) or heterogenized catalysts (*14, 15, 19*). The preparation and catalytic properties of ruthenium and rhodium complexes immobilized on polyacrylic acid (PAA) and other polycarboxylic ligands have also been reported previously (*6–8, 10*). The anchoring of a parent complex as $RhH(PPh_3)_4$ involves the formation of a carboxylate complex as for low-molecular-weight carboxylic acids:

$$Ⓡ\text{—COOH} + RhH(PPh_3)_4 \rightarrow Ⓡ\text{—COORh}(PPh_3)_x + H_2 + y PPh_3 \quad (1)$$

where $x + y = 4$; $x = 3$ when Ⓡ = alkyl or aryl groups; $x < 3$ when Ⓡ = polymeric chain.

In the formation of polymer derivatives a more extensive PPh_3 split-off generally occurred, with formation of potentially very active "coordinatively unsatured" metal species (*6, 10*). The carboxylate ligands, furthermore, have been found to bind strongly to the metal, with little or no leaching occurring under usual hydrogenation conditions (*7, 8, 10*).

Preparation of Polymer-Bound Complexes

Preliminary preparations of polymer-bound rhodium complexes using different COO/Rh molar ratios (20/1, 10/1, 4/1) by rapid addition of a dilute benzene solution of $RhH(PPh_3)_4$ to a refluxing dilute 2-propanol solution of PAA gave scarcely reproducible results. Hence, the above preparations were repeated carrying out the addition of the benzene solution dropwise in 4 h.

Analytical data and yields for the products obtained are given in Table 1.

Also in this case several drawbacks and complications were found:

(i) Unsatisfactory yields of polymer-bound carboxylate catalysts insoluble in the reaction medium. The amount of the soluble fraction increased on increasing the initial COO/Rh ratio. Part of the soluble products, however, became irreversibly insolubilized when the solvent was evaporated to dryness (sample (BP-20-SE).

(ii) Impossibility of increasing the metal loading beyond 9.6 wt.% (COO/Rh about 9), also by increasing the starting Rh/COOH ratio, due to the spontaneous precipitation of the polymer-bound system as soon as the plateau loading was reached (samples BP-10-HI and BP-4-HI).

(iii) Impossibility of regulating the P/Rh ratio of the metal units, i.e., the content of "coordinatively unsaturated" species, which is dependent on "local" and "instantaneous" coordinative situation and could therefore not be foreseen.

The use of other solvents or solvent mixtures, in which both the reagents are soluble (neat THF, or benzene/THF), or PAA is insoluble (benzene), did not improve the formation of polymer-bound systems, since they sometimes have a sticky consistency and contained metal species deprived of practically all the phosphine ligands (Table 1, samples B-20-SE, BT-20-HI, and T-20-SE).

Another problem related to the stability of the heterogenized systems was the observed change of chemical and physical properties during the separation operations (concentration of the solution, drying, washings, etc.) and catalytic experiments. This confirms the instability of "coordinatively unsaturated" metal species and the occurrence of interactions of metal sites with the excess of free –COOH groups of the matrix.

Therefore, in order to produce heterogenized catalysts which are easy to handle and with high and durable catalytic activity, we thought that a convenient way would be to add the reagents slowly to one another in solution and finally block the system through a crosslinking process of the polymer matrix.

In that respect, the free carboxylic functions of PAA not involved in coordination with the metal appeared suitable for the crosslinking of the system. Salts of divalent ions Ca^{2+} and Ba^{2+}, widely employed in aqueous medium, did not show any coupling ability in the reaction solvents. Aliphatic and aromatic diamines, such as hexamethylenediamine (HMD) and 4,4′-methylenedianiline (MDA), were found to be suitable for the crosslinking of PAA causing a rather immediate precipitation of the polymer from 2-propanol or THF solutions. In the former case, IR spectra of the solid product confirmed that part of the carboxylic groups was in the salt form (ν_{as}OCO at 1545 cm^{-1}) as expected for the formation of hexamethylenediammonium bridges:

$$2\textcircled{P}\text{—COOH} + H_2N(CH_2)_6NH_2 \rightarrow$$
$$\textcircled{P}\text{—COO}^- \; H_2\overset{+}{N}(CH_2)_6\overset{+}{N}H_2 \; {}^-\text{OOC—}\textcircled{P} \qquad (2)$$

Thus, the above preparations of polymer-bound complexes with different initial COOH/Rh ratios were repeated and the coupling agent (HMD) was added before the occurrence of any spontaneous precipitation. Analytical data and yields of the catalysts are given in Table 2.

The formation of highly insoluble products with satisfactory yields was attained using a COOH/HMD molar ratio of 2 (theoretical COO/N ratio of 10). The reactivity of the polymeric system toward the diamine strongly depends on the nature of the reaction medium: in benzene only about 1% of free carboxylic groups is involved in the crosslinking process, causing, however, the precipitation of about 70% of PAA (sample B-20-HMD). In more polar solvents, 6–13% of the carboxylic groups became coupled by the diamine (COO/N ratios 16–8, respectively). The highest coupling degree (COO/N ratio 8.0) has been obtained in the sample with the highest metal loading (sample BP-4-HMD), where practically all the diamine was consumed. This result might indicate that a certain "proximity effect" is operative under reaction conditions, by which carboxylic groups adjacent to the substituted one react preferentially.

As will be discussed later, the existence of direct rhodium–amine interactions seems very unlikely in all the cases investigated.

Catalytic Activity

The heterogenized complexes were used as catalysts in successive cycles for the hydrogenation and isomerization of pent-1-ene to obtain evidence for possible activation or deactivation phenomena. Catalytic data for polymer-bound complexes and the homogeneous model complex $Rh(OCOCHMe_2)(PPh_3)_3$ (IBUT) are shown in Fig. 1.

The heterogeneity in batch reactor experiments was almost complete for most of the polymeric catalysts. Only for the sample BP-10-RTI was a partial solubilization of the catalyst observed (heterogeneity about 74%) due to dissolution of a fraction of the polymeric system containing the metal always bound to the support (IR evidence).

Noncrosslinked and crosslinked catalysts exhibited a quite different behavior.

As a common feature noncrosslinked catalysts showed:

—lower activity than the model complex IBUT;

—change of activity upon recycle.

The former aspect is not surprising because, as a general rule, polymer-bound catalysts are less active than the corresponding low-molecular-weight analogs, due to the existence of steric factors reducing the availability of the active sites (*4*). In the first catalytic cycle, the system BP-20-SE, strictly comparable with the model complex having the same P/Rh ratio of 3, exhibits a TN_{150} about 5 times lower than IBUT.

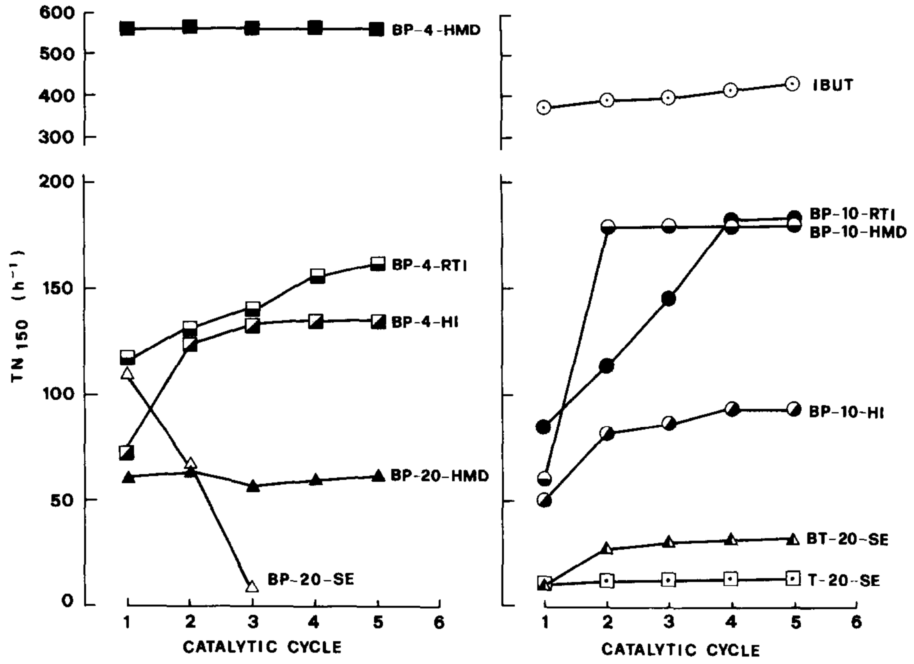

FIG. 1. Catalytic activity of homogeneous and heterogenized systems in the hydroisomerization of pent-1-ene at 50°C in 2-propanol (TN_{150} is referred to the overall pent-1-ene conversion).

The recycle of noncrosslinked systems may result either in an increase (BP-10-RTI, BP-10-HI, BP-4-RTI, and BP-4-HI samples) or a decrease (BP-20-SE sample) of the catalytic activity. This behavior cannot be interpreted simply on the basis of the different metal content or P/Rh ratio of the catalysts. The systems T-20-SE and BT-20-HI, having a very low P/Rh ratio, showed the lowest catalytic activities.

On the contrary, crosslinked catalysts gave

—activity sometimes higher than the model complex IBUT;

—constancy of activity upon recycle.

As a general trend, the catalytic activity for these systems was higher when the metal loading was higher, i.e., when the excess of free -COOH groups with respect to the metal centers was lower. The most striking results were obtained with the sample BP-4-HMD, showing a catalytic activity 4–5 times higher than that of the corresponding noncrosslinked derivatives BP-4-HI and BP-4-RTI, and also 1.4 times higher than that of the model complex IBUT.

Alongside a complete insolubility under catalytic conditions, this system showed no activation or deactivation on reuse. In addition to the high metal content, the relatively high concentration of crosslinking agent (COO/N = 8.0) of the BP-4-HMD system further reduces the possibility of formation of bis(carboxylato) rhodium species and sets the metal units apart from one another, both factors positively contributing to the noteworthy performance of this catalytic system.

Preactivation of the catalysts. Some catalyst samples were pretreated with hydrogen (2 MPA, 100°C, 2 h) and olefin (pent-1-ene/Rh molar ratio of 250) in order to eliminate or reduce the initial induction period and test their stability under more drastic reaction conditions.

Upon this treatment, most of the originally light-brown catalysts became dark or black, the formation of metallic rhodium being confirmed by the high increase of the hydrogenation activity, also of aromatic hydrocarbons (*20*).

On the contrary, the crosslinked catalysts did not darken under these conditions and showed an improved activity and a very high stability in catalytic reactions.

Selectivity in the catalysis. The selectivity data in successive runs for the soluble and heterogenized catalysts in the two parallel reactions of hydrogenation and isomerization, evaluated as pentane/pent-2-enes molar ratio at 50% pent-1-ene conversion, are reported in Table 3.

For noncrosslinked catalysts the selectivity was generally found to change on reuse, the isomerisation being progressively favored relative to hydrogenation. This is also the case for $Rh(OCOCHMe_2)(PPh_3)_3$, working in the homogeneous system, and for other heterogenized polycarboxylate catalysts previously studied (*6*, *10*).

The catalysts with higher metal loadings (BP-10-HI, BP-4-HI, BP-4-RTI, and BP-4-HMD) were more active in the hydrogenation, as the model complex in the first cycle, but, contrary to the soluble catalyst, did not appreciably change their selectivity upon recycle. A good preservation of the initial selectivity on reuse was a common feature of all the crosslinked systems.

In this case, the existence of interactions of the metal units with the coupling diamine can be reasonably ruled out since crosslinked and noncrosslinked systems with comparable COO/Rh and P/Rh ratios showed analogous initial selectivities.

Interpretation of the catalytic behavior from IR evidence. The analysis of the IR spectra of the heterogenized complexes, upon comparison with the spectrum of PAA (Fig. 2, spectrum A) and those of the samples recovered from catalytic experiments, gave the following information about the coordinated metal species:

—The attachment of the rhodium species to the polymer support takes place through the expected coordination of the carboxylate ligand, which is probably arranged in a bidentate fashion (Fig. 2, spectra D and E).

—The appearance of $OPPh_3$ frequencies after exposure of solid samples to air indirectly proved the presence of metal species in a "coordinatively unsaturated" situation, which are able to activate the dioxygen leading to autooxidation of coordinated PPh_3 (*21*).

—The BP-20-SE catalyst, deactivating

TABLE 3

Selectivity of the Catalytic Systems in Different Runs

Sample[b]	Rh (%)	COO/Rh	Selectivity[a]				
			1st run	2nd run	3rd run	4th run	5th run
$Rh(OCOCHMe_2)(PPh_3)_3$	10.37	1.0	1.1	0.7	0.6	0.5	
BP-20-SE	2.46	45.1	0.6	0.2			
BT-20-HI	4.17	31.1	0.5	0.3	0.2	0.2	
BP-10-HI	8.81	9.1	0.9	1.1	1.1	1.1	
BP-10-RTI	5.37	15.3	0.6	0.7	0.7	0.7	0.7
BP-4-HI	6.78	9.6	0.8	1.2	1.2	1.2	
BP-4-RTI	7.94	9.8	1.1	1.1	1.1	1.1	
BP-20-HMD	3.03	37.7	0.7	0.8	0.8		
BP-10-HMD	5.60	17.6	0.6	0.5	0.5	0.5	0.5
BP-4-HMD	7.02	9.8	1.2	1.1	1.2	1.1	1.1

[a] Evaluated as pentane (moles)/pent-2-enes (moles) at 50% pent-1-ene conversion.

[b] See footnotes of the preceding Tables.

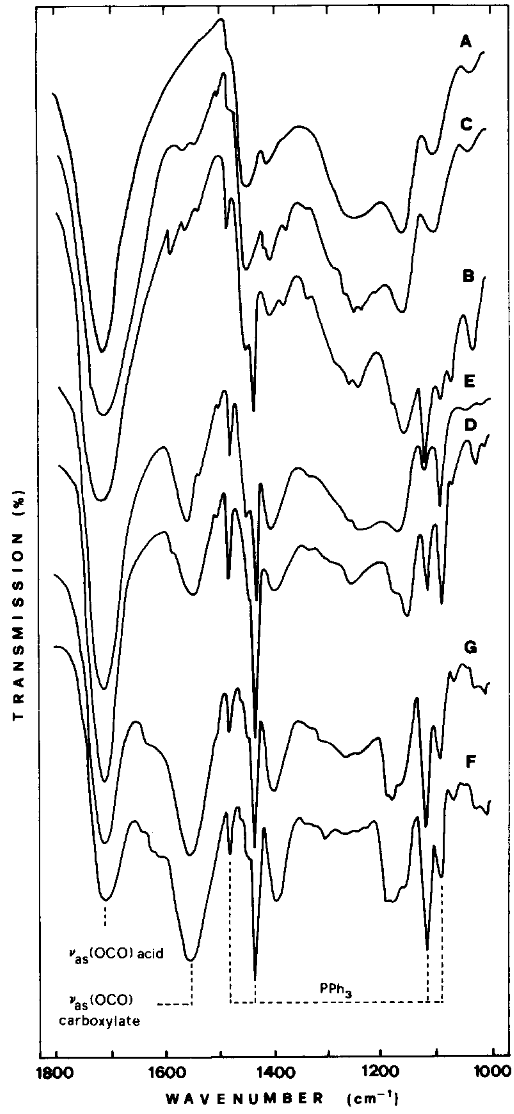

FIG. 2. IR spectra in the region 1800–1000 cm^{-1} of PAA (A) and of heterogenized catalysts: BP-20-SE before (B) and after (C) catalysis, BP-4-HI before (D) and after (E) catalysis, BP-4-HMD before (F) and after (G) catalysis.

upon recycle, showed an almost complete loss of PPh_3 under catalytic conditions (cf. spectra B and C of Fig. 2), whereas the decrease of PPh_3 was very limited for noncrosslinked systems showing activation on reuse (e.g., spectra D and E of BP-4-HI in Fig. 2). On the contrary, crosslinked catalysts, whose activity did not change on recycle, did not release PPh_3 appreciably under the same conditions (see, e.g., spectra F and G of BP-4-HMD in Fig. 2).

Catalyst samples were also treated in the solid state with CO under pressure (5 MPa, room temperature, 3 days) in order to generate carbonyl metal derivatives, whose CO stretching frequencies are sensitive to the metal environment.

The following features were observed:

—The model complex $Rh(OCOCHMe_2)(PPh_3)_3$ produced a monocarbonyl derivative [$\nu_{(CO)}$ at 1970 cm^{-1}, spectrum A in Fig. 3], whereas heterogenized complexes showed less resolved absorptions in the region 1950–2150 cm^{-1}, very similar for noncrosslinked (spectrum C in Fig. 3) and crosslinked systems (spectrum E in Fig. 3), and suggesting the presence of at least two main types of coordinative situations of the metal species.

—Samples of the model complex and of noncrosslinked heterogenized catalysts recovered after catalytic runs and treated as above (spectra B and D, respectively, in Fig. 3) showed a different pattern of absorptions with respect to original samples with a shift of $\nu_{(CO)}$ toward higher wavenumbers, diagnostic of an increased acidity of the metal centers.

—No substantial change in the spectra of crosslinked systems recovered after catalysis was observed (spectrum F, Fig. 3) with respect to the original sample (spectrum E).

The above spectroscopic evidence allows us to rationalize the catalytic properties of the heterogenized systems chiefly in terms of the P/Rh ratio and mobility of the macromolecular chains of the polymer matrix. According to previous findings (*6*, *7*), we can attribute the activation phenomena shown by most of the noncrosslinked catalysts to a progressive formation of new "coordinatively unsaturated" metal species by a partial loss of coordinated PPh_3. However, when PPh_3 is released to too large an extent, as occurs for the BP-20-SE system, this results in a decrease of the catalytic activity, the presence of the phosphine ligand in the coordination sphere of

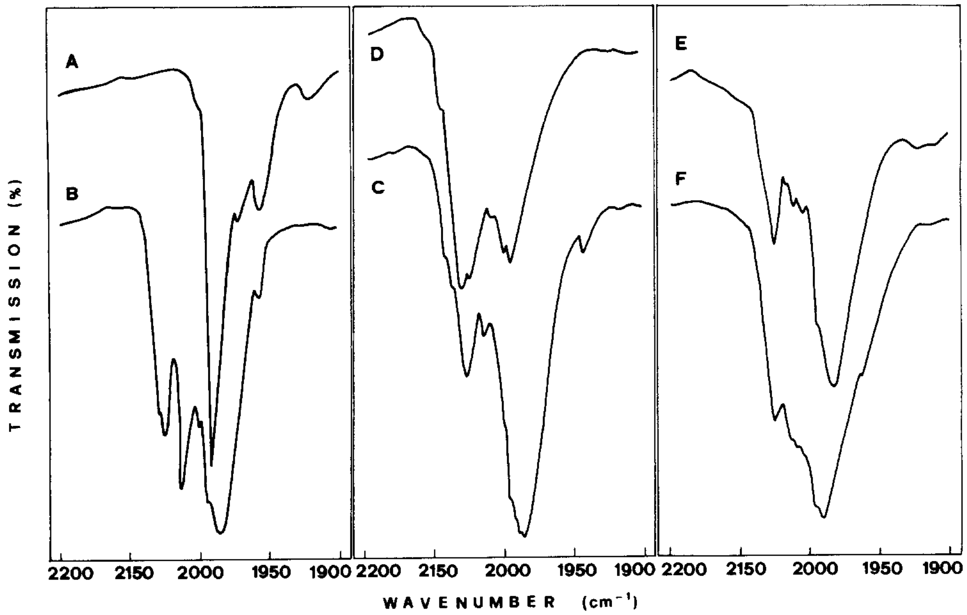

FIG. 3. IR spectra in the region 2200–1900 cm^{-1} of homogeneous and heterogenized catalysts treated in the solid state with CO under pressure: IBUT before (A) and after (B) catalysis, BP-10-RTI before (C) and after (D) catalysis, BP-4-HMD before (E) and after (F) catalysis.

the metal being positive in promoting the activation of molecular H_2 and preventing the deactivation of metal sites (*22*).

Therefore, we can conclude that compromise conditions of relatively low initial P/Rh ratios and slight PPh_3 release under reaction conditions are key requirements to obtain the best catalystic performance.

In this light, the good catalytic properties of the crosslinked catalysts may be attributed to the unusual stabilization of metal centers in a "coordinatively unsaturated" situation, this allowing an overcompensation for the negative effect of the polymeric ligand, and in the preservation of the metal environment under catalytic conditions, both due to the rigid network of the polymer matrix avoiding PPh_3 split-off and further interactions of the metal centers with competitive ligands.

CONCLUSIONS

This study demonstrates that the catalytic performance of a polymer-bound catalyst can be strongly improved through an optimization of the preparative procedure and modification of the properties of the support by a crosslinking process involving the reactive groups of the polymer.

When the polymer has a high content of functional groups, as, for example, is the case with polyacrylic acid, a high dispersion of the metal units within the reactant does not produce positive effects on the catalytic activity of the anchored metal species, contrary to what generally occurs with inorganic supports. In fact, the mobility of the polymer chains allows frequent interactions of the metal units with the free functional groups, resulting either in an activation through the displacement of part of the ligands initially present (PPh_3), or in a deactivation through a polycoordination to the matrix, or finally in a weakening of the stability of the catalyst which is easily reduced to metal. In this context, both the increase of the metal loading on the polymer support and blocking of structural situations achieved in solution by a crosslinking of the matrix give a positive effect. This latter procedure, avoiding the interactions of the metal sites with the free functions of the polymer and generating a rigid network around the active centers, may result in the attainment of more active metal species and in preservation of their properties upon prolonged use.

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