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Olefin oligomerization / polymerization reactions in the presence of gaseous H_2 / CO over rhodium catalysts

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Catalysts prepared by impregnation of the molecular species $H(CO)Rh[P(C_6H_5)_3]_3$ or $ClRh[P(C_6H_5)_3]_3$ with the aluminophosphate micropore VPI-5 have been found to catalyse the conversion of sodium 4-styrenesulfonate in aqueous solution in the presence of gaseous H_2 / CO mixture into the expected aldehyde hydroformylation product together with a substantial quantity of olefin polymer. Reaction in the presence of H_2 in the gas phase gave the expected olefin hydrogenation product but no polymer, while in the presence of CO or N_2 in the gas phase no reaction product of any sort could be found. The addition of a small quantity of hydroquinone as a radical scavenger to the reaction in the presence of gaseous H_2 / CO had no effect, indicating that the polymerization process did not occur by a free radical mechanism. It is suggested that polymerization occurs via a coordinated ligand insertion mechanism, and evidence suggests that the catalytic sites are those rhodium complex molecules which are externally accessible either at VPI-5 pore mouths or otherwise are located at the VPI-5 external surface, and which have been modified, probably by a ligand exchange process involving VPI-5 framework atoms.

Keywords: olefin polymerization in water, hydroformylation, rhodium catalysts, VPI-5, Rh complexes in VPI-5, supported Rh complexes

The use of the organometallic rhodium species $H(CO)Rh[P(C_6H_5)_3]_3$ (A) and $ClRh[P(C_6H_5)_3]_3$ (B) as homogeneous catalysts in non-aqueous media for hydroformylation or hydrogenation reactions with olefins is well known [1]. However, in the course of studying these reactions in aqueous media using water-wettable catalysts prepared by the incorporation of (A) or (B) into the pores of the aluminophosphate micropore VPI-5, together with a water-soluble olefin reactant such as sodium 4-styrenesulfonate, we observed that an olefin oligomerization/polymerization reaction could be an important process under hydroformylation conditions. The purpose of this communication is to outline the main features of this unusual polymerization reaction. We have never observed any polymerization [1] when (A) or (B) was used as a homogeneous catalyst in non-aqueous solution for hydroformylation or hydrogenation reactions, nor have we been able to find reference to such in the literature.

There exists, of course, a sizeable literature concerning the use of various (non-Rh) organometallics as olefin polymerization catalysts such as aryl or allyl derivatives of nickel [2], chromium [3] or cobalt [3,4], but previous work describing rhodium catalysts for olefin polymerization appears to be confined to the use of Rh^{3+} salts such as rhodium trichloride or rhodium trinitrate in an essentially aqueous solution, or the use of a rhodium complex formed in situ from Rh^{3+} and one of several diolefin ligands [5,6], these polymerization reactions being carried out in the absence of H_2 or H_2/CO. These catalyst systems based on the use of Rh^{3+} species pose the problem of solubility incompatibility between the Rh^{3+} species and the water-insoluble reactant, a problem that has been frequently addressed by carrying out the reaction in an emulsion, using a surface active agent such as sodium dodecylbenzenesulfonate [5].

In the present work, the VPI-5 was prepared and dehydrated using the optimal protocols described previously [7]. Compound (A) or (B) (Aldrich) was introduced into the dehydrated VPI-5 from solution in dry, degassed benzene with stirring for 24 h at room temperature. The impregnated VPI-5 was recovered by filtration, washed with dried, degassed benzene (10 ml for 200 mg VPI-5), and dried under vacuum at room temperature. All manipulations were carried out under dried, oxygen-free nitrogen. As described elsewhere [8], under the above impregnation conditions, 200 mg of VPI-5 can sorb up to about 32 mg of (A) or (B) into the pores. However, most of the catalysts used in the present work contained 8 mg of (A) or (B) impregnated into 200 mg of VPI-5.

Because of the closeness of fit between these guest molecules and the VPI-5 pore walls, these guest molecules are relatively strongly sorbed (presumably by van der Waals interactions): thus, they are largely resistant to removal by washing with benzene (10 ml for 200 mg

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[1] For simplicity, in the rest of this paper, we use the term "polymerization" to include the possible formation of lower molecular weight oligomers.

VPI-5) at room temperature, although they may be removed by boiling benzene.

Reactions were carried out in a Parr 100 ml stainless steel autoclave fitted with a glass liner. Using manipulations under dried, oxygen-free nitrogen, a sample of (A)/VPI-5 (208 mg) or of (B)/VPI-5 (208 mg) was placed in the autoclave together with sodium 4-styrenesulfonate (300 mg) and 10 ml of degassed water. After closure, the autoclave was pressurized to 400 psi (in most cases) with the appropriate gas (cf. table 1), and was then heated with stirring at a temperature in the range 20–90°C for (in most cases) 20 h. After reaction, the autoclave was cooled to room temperature, the catalyst separated by filtration, washed with water (3 × 5 ml), and the filtrate was evaporated to dryness at room temperature under vacuum. The recovered solid residue was analysed by ^{1}H NMR in D_2O, infrared spectroscopy, and negative ion electrospray mass spectrometry. The data for the reaction product were also compared with corresponding data obtained from a commercial sample of sodium 4-styrenesulfonate polymer (Aldrich, stated molecular weight ca. 70 000).

Substantial amounts of polymer were produced using either (A)/VPI-5 or (B)/VPI-5 catalyst in the presence of gas phase H_2/CO mixture, as shown in table 1 (cf. runs 1–4; 9 and 10). Further data in table 1 show that no polymer was produced using either catalyst in the presence of gas phase H_2 (i.e. no CO), the reaction then being confined to hydrogenation, nor was any polymer produced (nor any other product) in the presence of gas phase N_2 or CO (using (A)/VPI-5 catalyst) (cf. table 1, runs 7 and 8).

Additionally, it was found that attempted reactions (90°C, 20 h, H_2/CO) in the presence of VPI-5 (200 mg) alone in H_2O, or (A) (8 mg) alone in H_2O, gave zero conversion, while the presence of both VPI-5 (200 mg) and (A) (8 mg) added separately to the H_2O (i.e. without impregnation of the complex into the VPI-5) gave only trace conversion ($< 5\%$). The use of $RhCl_3{\cdot}3H_2O$ (4.5 mg) in H_2O at 50°C for 20 h with 400 psi H_2 gave no polymer, but 100% conversion by hydrogenation. It was also found that reaction with the catalyst compound (A)/VPI-5 with H_2 at 15 psi pressure (cf. table 1, run 6) gave, as expected, a reduced conversion compared with that obtained at 400 psi H_2 pressure, but the reaction product still contained no polymer.

Analysis by GC of the gas phase after reaction at 70°C using compound (A)/VPI-5 with H_2/CO, gave no evidence for the presence of C_1–C_6 hydrocarbons.

In all cases where hydroformylation product was formed (cf. table 1, runs 1–6, 9–12), it consisted of the appropriate branched aldehyde (sodium 4-(1′-formylethyl)benzesulfonate and the corresponding branched aldehyde hydrate.

A comparative study was made using a rhodium complex catalyst formed in situ between Rh^{3+} (from 2.5 mg $RhCl_3{\cdot}3H_2O$) and 5 mg of the ligand TPPMS (triphenylphosphine monosodium sulfonate) in 10 ml H_2O, with 300 mg of reactant sodium 4-styrenesulfonate and H_2/CO (molar ratio 1/1) at 400 psi: reaction for 20 h at 70°C. Reactant conversion was 100%, yielding aldehyde and aldehyde hydrate (molar ratio approximately 1/2) but no polymer.

The ^{1}H NMR spectrum (in D_2O, referenced to TMS) of the reaction products obtained using catalyst (A)/VPI-5 under hydroformylation conditions (e.g. run 2,

Table 1

Reactions of sodium 4-styrenesulfonate in aqueous solution using $H(CO)Rh[P(C_6H_5)_3]_3$/VPI-5 or $ClRh[P(C_6H_5)_3]_3$/VPI-5 catalyst [a,b]

Run No.	Catalyst	Reaction conditions		Gas phase (psi)	Reactant conversion (%)	Product selectivity (%) [d]	
		T (°C)	time (h)			polymer	other products
1	(A)/VPI-5	70	20	H_2/CO (400) [c]	70	57	43 [e]
2	(A)/VPI-5	90	20	H_2/CO (400) [c]	100	80	20 [e]
3	(A)/VPI-5	80	28	H_2/CO (400) [c]	83	90	10 [e,f]
4	(A)/VPI-5 [h]	80	28	H_2/CO (400) [c]	83	90	10 [e,f]
5	(A)/VPI-5	50	20	H_2 (400)	52	0	100 [g]
6	(A)/VPI-5	50	20	H_2 (15)	37	0	100 [g]
7	(A)/VPI-5	80	20	CO (400)	0	0	0
8	(A)/VPI-5	80	20	N_2 (400)	0	0	0
9	(B)/VPI-5	70	20	H_2/CO (400)	50	56	44 [e]
10	(A)/VPI-5	90	20	H_2/CO (400)	60	82	18 [e]
11	(A)/VPI-5	50	20	H_2 (400)	100	0	100 [g]
12	(A)/VPI-5	20	20	H_2 (400)	5	0	100 [g]

[a] Sodium 4-styrenesulfonate (300 mg), H_2O (10 ml), catalyst (208 mg) total, containing 200 mg VPI-5 and 8 mg Rh compound (A) or (B).

[b] $H(CO)Rh[P(C_6H_5)_3]_3 \equiv$ (A); $ClRh[P(C_6H_5)_3]_3 \equiv$ (B).

[c] H_2/CO molar ratio = 1/1.

[d] Selectivity as relative numbers of reactant molecules entering indicated products.

[e] Branched aldehyde plus corresponding hydrate.

[f] Analysis by GC of the gas phase after reaction gave no evidence for the presence of C_1–C_6 hydrocarbons.

[g] Sodium 4-ethylbenzene sulfonate.

[h] Same reaction conditions as run 3 except for the addition of 1 mg hydroquinone to reaction mixture.

table 1) is shown in figure 1 together, for comparison, with the corresponding ^{1}H NMR spectrum obtained from the Aldrich commercial polymer. The main, relatively broad, peaks are very similar in the two cases, with chemical shifts (ppm) indexed as follows: 7.2–8.6 (Ar**H**, *m*- and *p*-); 5.8–7.1 (Ar**H**, *o*-); 0.8–2.5 ($\mathbf{CH_2}$ and **CH**).

The fine structure to be seen in the spectrum from the present work is due to hydroformylation products. The broad polymer peaks shown in figure 1 agree very well with previously published ^{1}H NMR spectra for polystyrene taken in $CDCl_3$ [9]. It should be noted that the ^{1}H NMR spectrum for our product in figure 1 contains no evidence for a methyl group which would be present in branched polymer (this absent methyl NMR peak would be a singlet at about 1.2 ppm). We therefore conclude that our polymer product is entirely linear. The fact that such hydroformylation product as was formed in our work was *branched* aldehyde (and the corresponding hydrate) is of no relevance in relation to the formation of *linear* polymer since the two processes are quite distinct (cf. later discussion).

The infrared spectra obtained from the reaction product of the present work using catalyst (A)/VPI-5 under hydroformylation conditions and the corresponding infrared spectrum from the commercial Aldrich sodium 4-styrenesulfonate polymer are shown in figure 2. The spectral similarity of the two samples is clear, from which we infer the basic similarity of the two materials. There was no infrared evidence for incorporation of CO into the polymer.

Negative ion electrospray mass spectra were obtained in aqueous methanol solution from both our product and from the commercial Aldrich polymer. Although the complexity of the mass spectra is such as to defy detailed analysis, the two mass spectra were broadly quite similar, both occurring in the m/z range 500–1500 (except some monomer peaks), the main difference being the relatively greater concentration of line intensity in the m/z range 600–1000 for the commercial polymer.

Experiments showed that although a small proportion of the rhodium was lost into the aqueous phase from the VPI-5 under reaction conditions, this rhodium in aqueous solution had negligible activity for hydrogenation, hydroformylation or polymerization, so that the observed catalytic activity for both (A)/VPI-5 and (B)/VPI-5 resided in the rhodium species associated with the VPI-5. Thus the catalyst (B)/VPI-5 used for hydrogenation under the conditions of run 11, table 1 (giving 100% reactant conversion) underwent a loss of ca. 6% rhodium into the aqueous phase: this rhodium-containing aqueous phase had negligible catalytic activity, but the recovered (B)/VPI-5 catalyst gave 100% reactant conversion under the conditions of run 11, table 1. Similarly, the catalyst (A)/VPI-5 under hydroformylation conditions ($H_2CO = 1/1$; 400 psi, 20 h; 60°C; total reactant conversion 10%) underwent a rhodium loss of ca. 4%, and the rhodium-containing aqueous phase had negligible catalytic activity under similar reaction conditions.

There is evidence [8] to support the view that, with catalysts (A)/VPI-5 and (B)/VPI-5, most of the rhodium species are located within the micropore channels. On this basis, one would be led to conclude that the catalytic activity would be mainly confined to those rhodium species which are directly accessible via a channel mouth

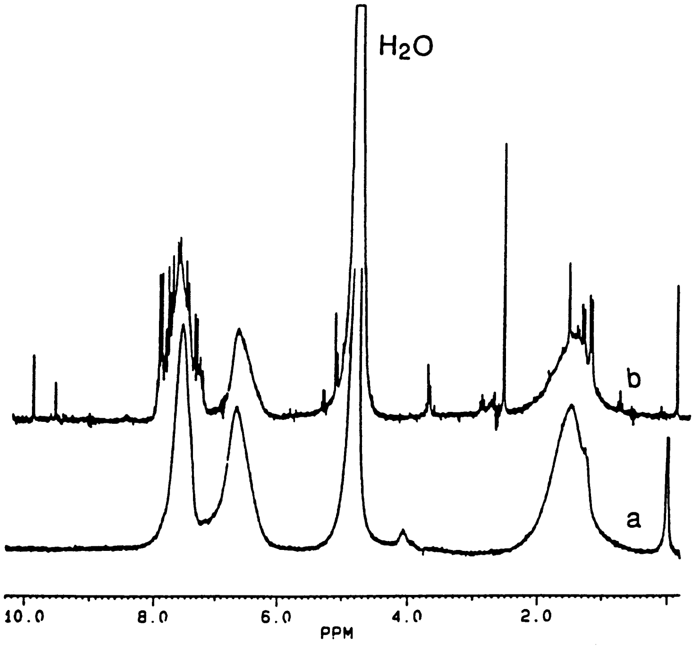


Figure 1. ^{1}H-NMR spectra in D_2O of (a) commercial sodium 4-styrenesulfonate polymer (Aldrich); and (b) product obtained using (A)/VPI-5 under hydroformylation conditions (e.g. run 2, table 1) with sodium 4-styrenesulfonate in H_2O.

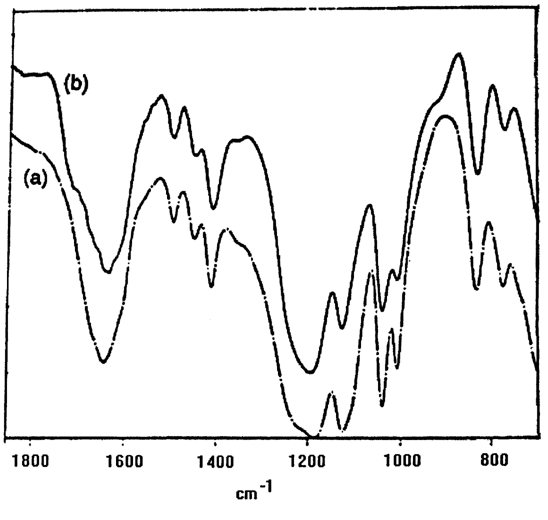


Figure 2. Infrared spectra of (a) commercial polymer from sodium 4-styrenesulfonate (Aldrich), and (b) obtained from use of compound (A)/VPI-5 catalyst with sodium 4-styrenesulfonate in water under hydroformylation conditions (e.g. run 2, table 1).

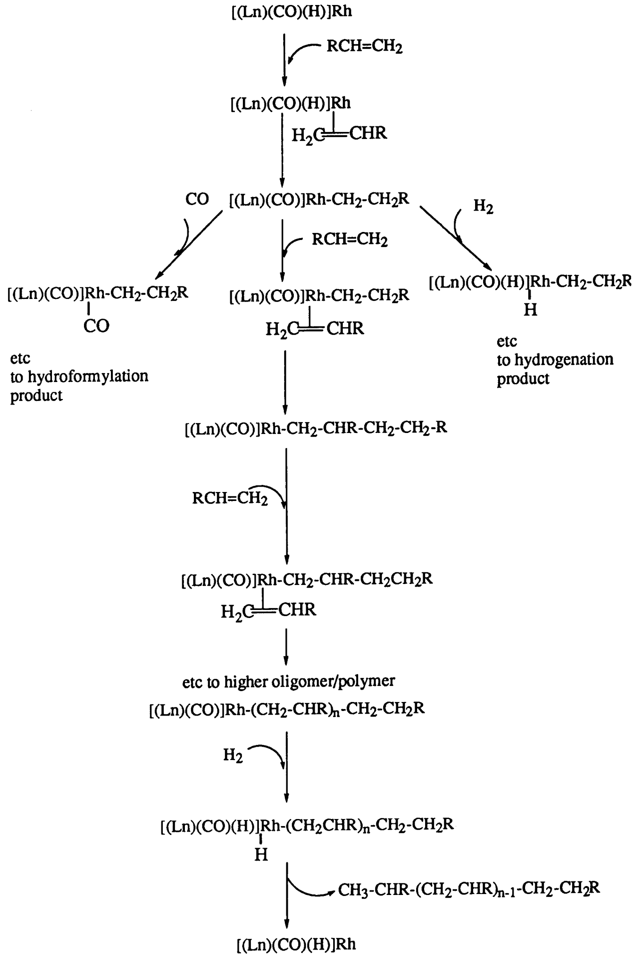
since VPI-5 has a unidirectional, non-intersecting, channel structure, and a reactant molecule such as sodium 4-styrenesulfonate would only be able to reach a rhodium species to which it had direct and unimpeded channel access. However, the size of the oligomer/polymer product molecules is, relative to the VPI-5 pore size, such that most of the chain growth process must occur at rhodium species located either at channel mouths or otherwise at the external surface of the VPI-5 particles. We currently have no way of distinguishing between these alternative locations.

Finally, we turn to the question of a possible oligomerization/polymerization reaction mechanism. The absence of any reduction in reactant conversion consequent upon the addition of hydroquinone (a radical quencher) (cf. table 1, run 4) leads to the conclusion that polymerization does not in these cases occur via a free radical route. A similar conclusion was previously reached with respect to olefin polymerization using aqueous Rh^{3+} species as catalyst [5a].

From the data given previously, it appears that, (a) polymerization is competitive with hydroformylation when a H_2/CO gas phase is used, provided the catalytically active Rh complex species are located with VPI-5; (b) when the gas phase is H_2 the reaction is dominated exclusively by hydrogenation which is more facile than hydroformylation; (c) no polymerization is possible in the absence of at least some H_2 (cf. table 1, runs 7 and 8); (d) the presence of water as such has little or no effect on the propensity of the reaction with H_2/CO to give hydroformylation rather than polymerization since the use of a TPPMS/Rh catalyst in water gave only hydroformylation and no polymerization.

We suggest that polymerization occurred in the present work via a coordinated ligand insertion mechanism which has a formal analogy to olefin hydroformylation in that both involve ligand insertion processes. Reaction scheme 1 outlines the main steps. According to reaction scheme 1, catalytic oligomerization/polymerization would require at least *some* hydrogen to allow the catalytic cycle to be completed. If, as shown, the product is a saturated hydrocarbon, this is generated at the final step in the sequence by reductive elimination from a species which has previously been formed by reaction with H_2 by oxidative addition.

On the basis that polymerization is, in principle, competitive with hydroformylation and hydrogenation, but with the latter effectively quenched by CO, we suggest that under the present reaction conditions the reason for the relative prominence of the polymerization process must be sought in the nature of the active catalyst. For polymerization, we suggest that incorporation of (A) or (B) with VPI-5 results, at least with those species which provide the active catalytic sites, in a modification to their molecular structure, possibly by a ligand exchange process involving framework atoms of the VPI-5. This proposal is consistent with the observation [8] that some



Scheme 1. For clarity, only linear products/intermediates are shown, but this is in agreement with NMR data for polymer (cf. text). Ln represents one or more ligands.

triphenylphosphine is lost from the rhodium complex molecules in the process of impregnation with VPI-5, although, of course, it is known [10] that compounds (A) or (B) undergo a small degree of spontaneous dissociation with the loss of triphenylphosphine molecules in benzene solution.

Such a ligand exchange process would be expected to affect the electronic properties of the central metal atom, and it is already known that insertion reactions of the type involved here are very sensitive to electronic factors of this sort [1,11].

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