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THE HYDROGENATION OF OLEFINS USING A POLYMER SUPPORTED RUTHENIUM COMPLEX

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Summary

$RuCl_2(PPh_3)_3$ has been attached to a phosphinated polymer support (phosphinated polystyrene crosslinked with 2% divinylbenzene) and the reagent converted to the polymer supported analogue of $RuClH(PPh_3)_3$ in the presence of base. The polymer supported catalyst efficiently hydrogenates terminal olefins under ambient conditions. Hydrogenation of 1-hexene has revealed that the reaction rate is proportional to [Ru], $[H_2]$ and [olefin]/(1 + [olefin]). The polymer support environment allows for selectivity in olefin hydrogenation and under suitable reaction conditions short chain terminal olefins are hydrogenated more rapidly than long chain terminal olefins. The extent of metal loading on the polymer and the reaction solvent composition also influence the reaction selectivity and these effects are discussed.

Introduction

The hydrogenation of olefins catalysed by soluble ruthenium complexes was first described 20 years ago [1]. In the report acidic solutions containing chlororuthenate (II) complexes were found to reduce activated olefins at 65—90°C under 1 atmosphere H_2. A Ru^{II} hydride complex, analogous to *trans*-$RuXH(diphosphine)_2$ (X = halogen) [2], was suggested to be the catalytically active species in the reaction. Six years later the role of Ru—H complexes in catalytic olefin hydrogenation reactions was conclusively demonstrated by Wilkinson et al. [3] for reaction solutions containing $RuCl_2(PPh_3)_3$. The complex $RuCl_2(PPh_3)_3$ readily forms $RuClH(PPh_3)_3$ in the presence of hydrogen (and base) and mechanistic information on catalytic reactions involving this and similar complexes [4—6] has been reviewed by James [7—9].

A problem associated with the use of catalysts of the type $RuXH(PPh_3)_3$ (X = Cl, COOR), and with most homogeneous catalysts, is the difficulty in separating the products and reactants from the catalyst at the end of the reac-

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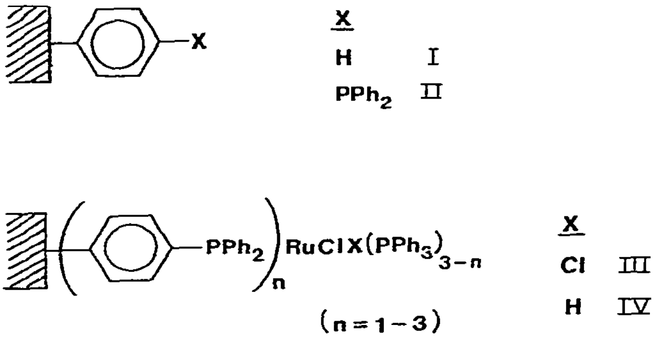

Fig. 1. Structures of the polymers and polymer supported reagents.

tion. For expensive metals such as Ru this becomes a problem of economic significance and could outweigh any benefits obtained from using a homogeneous rather than a heterogeneous catalyst. A number of approaches to solve this problem have been attempted over the past decade, one of which is the use of polymer supported catalysts [10]. We have thus undertaken a study of a polymer supported ruthenium complex, analogous to the Wilkinson catalyst, $RuClH(PPh_3)_3$ to investigate the advantages and/or disadvantages of using a polymer support on the catalytic hydrogenation of olefins. The polymer support used was polystyrene crosslinked with 2% divinylbenzene, I (Fig. 1). The reactions were carried out in 1/1 ethanol/benzene mixtures and for comparison catalytic reactions using the homogeneous catalyst $RuClH(PPh_3)_3$ were also recorded in this solvent system.

$RuClH(PPh_3)_3$ has poor solubility characteristics [4]. It was hoped that attachment of the catalyst to a polymer support would overcome the solubility problem and result in increased hydrogenation activity.

Experimental

$RuCl_2(PPh_3)_3$ was prepared by the literature method [11]. The phosphinated polymers, II, were prepared from polystyrene crosslinked with 2% divinylbenzene, I, (Dow Chemicals 200—400 mesh or Strem Chemicals, 20—60 mesh), as described previously [12]. Olefins (various sources) were passed down a short silica gel (Merck, Kieselgel 60) column before use.

X-ray fluorescence spectrometry was performed on a Phillips P.W. 1410 X-ray fluorescence spectrometer (P, Cl, Ru). Elemental analyses were carried out by the Microanalytical Laboratories, C.S.I.R., Pretoria (Table 1).

Preparation of III

$RuCl_2(PPh_3)_3$ (1.0—6.0 g) was added to the phosphinated polymer, II, (5 g) in dry, degassed benzene and the solution stirred under nitrogen at room temperature for 20—25 days. Solvent was then removed in vacuo, and the solid reactants transferred to a soxhlet extractor and extracted under nitrogen with a 1/1 benzene/ethanol mixture. When the extraction was complete the thimble was transferred to an appropriate flask and dried in vacuo. Analytical data and

TABLE 1

ANALYTICAL RESULTS FOR THE POLYMER SUPPORTED METAL COMPLEXES USED IN THIS STUDY

Sample	Before metallation (%) [a]		After metallation (%) [b]			
	Br	P	Br	P	Cl	Ru
R1	2.5	11.5	1.77	0.6	0.3	0.65
R2	6.0	40.0	2.23	2.31	1.58	2.46
R3	3.5	42.5	1.81	3.17	2.40	3.37
R4	1.5	13.5	—	2.27	1.95	2.76
R5	1.5	28.0	—	2.32	2.45	3.20

[a] Data refer to % rings substituted by Br or PPh_2. The data were calculated from mass spectral results [12]. [b] Mass %.

the extent of ring substitution of the prepared samples are listed in Table 1. The beads thus obtained were brown and in general, the higher the % ruthenium attached to the polymer, the darker the polymer beads.

Hydrogenation of 1-hexene

All hydrogenation reactions were performed in a 3-necked hydrogenation flask (Fig. 2) attached to an hydrogenation apparatus. Solvent (~20 ml, 1/1 benzene/ethanol) together with triethylamine (0.20 ml) were added to the 3-necked flask. Catalyst (100—300 mg) was weighed into a glass vial and placed in the side arm of the hydrogenation flask. This flask was then connected to a vacuum line and degassed by two freeze/thaw cycles. The flask was then transferred to the hydrogenation apparatus and at the same time immersed in a thermostatically controlled water bath (±0.1°C) and the apparatus was purged/filled with hydrogen. The tap connecting the hydrogenation flask to the hydrogenation apparatus was then opened and the whole system was purged/filled with hydrogen three times.

The side arms of the flask was then inverted and the catalyst added to the solvent mixture. The mixture was allowed to equilibrate with stirring for 30 minutes. Olefin (degassed by freeze/thaw cycles) was added by microsyringe,

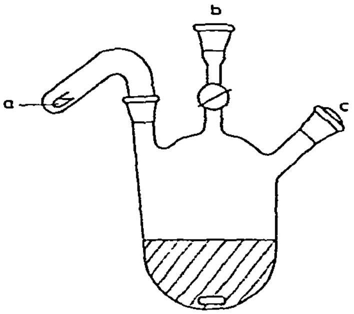

Fig. 2. Diagram of the hydrogenation vessel, (a) vial containing catalyst; (b) vessel connected to hydrogenation apparatus via B14 joint; (c) rubber septum.

through the rubber septum, to the hydrogenation apparatus. The hydrogenation reaction was monitored by hydrogen uptake at a pressure of ±620 mmHg (0.82 atm).

Unless otherwise stated all kinetic data refers to the following conditions: temperature, 30.0 ± 0.1°C; stirring rate, 500 rpm; solvent system, ~20 ml of 1/1 benzene/ethanol (96%); NEt_3, 0.20 ml. All rate data refer to the initial rates of the reaction, and repeat experiments indicated an error of <5% in the rate data.

Results and discussion

The reaction between $RuCl_2(PPh_3)_3$ and II occurs slowly at room temperature to give the required product III. This reagent can be transformed into the required catalyst, IV, in the presence of base and hydrogen [3]. To date we have been unable to obtain definitive evidence for the structures of III and IV. However, a consideration of the analytical data for polymer III (Table 1) suggests that for all 5 polymer reagents studied the ratio of Ru to Cl is ~1/2 and the Ru to P ratio is ~1/3. This strongly suggests that III is the polymer supported equivalent of $RuCl_2(PPh_3)_3$ with $n = 3$ (Fig. 1). The possibility that dimerization of IV might occur in a polymer environment to yield $[RuClH(PPh_3)_2]_2$ [13,14], as has been found for polymer supported $RhCl(PPh_3)_3$ [15], cannot at this stage be ruled out. Evidence for IV having the structure proposed is also provided by elemental analysis data of a polymer sample after use as a catalyst. The used catalyst was analysed by X-ray fluorescence and gave a Ru/Cl/P ratio of 1/1/3. Further evidence for the structure of IV is provided by its method of synthesis and its reactivity towards oxygen (vide infra). IR data have been of limited assistance in establishing the structures of III and IV.

Prior to a thorough kinetic investigation of the hydrogenation reaction we investigated two phenomena which could affect our results. The first of these was the time required to form the metal hydride IV from III. By adding the olefin to the reaction solvent prior to the addition of catalyst we were able to obtain the minimum amount of time required for conversion of III into IV. For the hydrogenation of 1-hexene under our reaction conditions this was found to be 6 min for the homogeneous catalyst, 15 min for III (200—400 mesh beads), and 30 min for III [20—60 mesh beads].

The second phenomenon was the effect of the solvent ratio on the reaction. The results of this study are shown in Fig. 3 and Table 2. For the homogeneous catalyst (with or without base), the reaction rate increases with the % ethanol i.e. with increasing solvent polarity in the benzene/ethanol mixture. However, the polymer supported catalyst shows a distinct maximum at ~50% ethanol content. This arises from two competing effects: the ability of the polymer to swell in different solvents and the effect of solvent polarity on the reaction [11]. The former is due to benzene which makes accessibility to the active sites within the bead easier while the ethanol is required for conversion to, and solubilization of the hydride [4,16]. The rate of the reaction for catalyst IV is thus a compromise between the two effects. This phenomenon has already been observed with other polymer supported catalyst systems [17,18]. The rate law for the hydrogenation of 1-hexene was evaluated by varying the olefin,

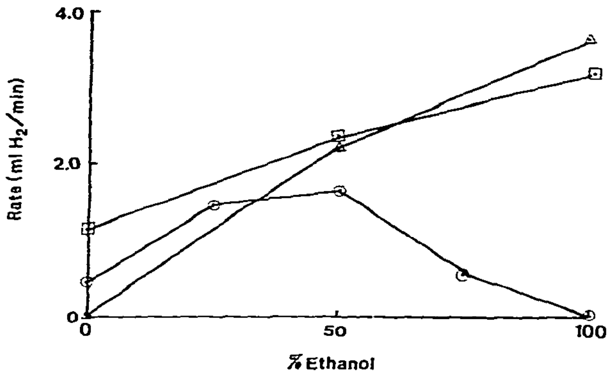

Fig. 3. Effect of varying benzene/ethanol solvent ratio on the hydrogenation reaction. Data refer to: △ $RuCl_2(PPh_3)_3$ — no base added, □ $RuCl_2(PPh_3)_3$ — 0.20 ml NEt_3, ⊙ sample R5. (Hydrogenation of 1-hexene).

ruthenium and hydrogen concentrations in the catalytic reaction.

Effect of olefin concentration. The effect of varying [olefin] on the reaction rate is shown in Table 3 and Figs. 4 and 5. Figure 4 indicates that an increase in olefin concentration results in a rate increase, but that at high olefin concentrations the rate reaches a limiting value. This limiting value is due to a limiting ruthenium concentration and not due to a lack of dissolved hydrogen; increasing [Ru] at a specific [olefin] results in an increased reaction rate. A plot of 1/rate versus 1/[olefin] gives a straight line (Fig. 5) which suggests that the rate law is of the form, rate = A[olefin]/(B + [olefin]) (A, B constants). This is the same form of the rate law as found for many other homogeneous [19] and polymer supported [17] catalytic systems, including $RuClH(PPh_3)_3$ in benzene/ethanol (see Fig. 4) and dimethylacetamide [7].

From the plot of 1/[olefin] versus 1/rate (Fig. 5) it is possible to obtain the theoretical maximum rate of hydrogenation under our reaction conditions. Increasing the stirring rate, temperature or H_2 pressure will increase this value but an increase in [Ru] or [olefin] has no effect on this maximum rate. The

TABLE 2

EFFECT OF SOLVENT RATIO ON THE HYDROGENATION OF OLEFINS [a]

Ethanol (ml)	Benzene (ml)	Rate of hydrogenation (ml min^{-1}) [b]		
		Sample R5	$RuCl_2(PPh_3)_3$	Styrene [c] / 1-hexene
0	19.2	0.47	1.08	0.64
4.8	14.4	1.46	—	0.59
9.6	9.6	1.62	2.39	0.50
14.4	4.8	0.45	—	0.47
19.2	0	0	3.22	—

[a] Reaction conditions: 0.23 M 1-hexene, 0.20 ml NEt_3. [b] Hydrogenation of 1-hexene. [c] Ratio of rates of the hydrogenation reaction under identical experimental conditions.

TABLE 3

HYDROGENATION OF 1-HEXENE: EFFECT OF VARYING CATALYST AND OLEFIN CONCENTRATIONS

Catalyst (mg)	Olefin (ml)	1/olefin (l mol^{-1}) [a]	Rate (ml min^{-1})	1/rate (sec mol^{-1} × 10^6)
100 [b]	0.30	8.34	0.44	2.73
	0.40	6.25	0.58	2.07
	0.60	4.17	0.76	1.58
	0.80	3.13	0.90	1.33
150 [b]	0.12	20.17	0.43	2.79
	0.20	12.75	0.46	1.82
	0.30	8.54	0.87	1.38
	0.40	6.44	1.20	1.00
	0.60	4.33	1.45	0.83
	0.80	3.28	1.33	0.90
300 [b]	0.25	10.23	1.58	0.76
	0.40	6.44	1.91	0.63
	0.80	3.13	2.37	0.51
	2.00	1.25	2.56	0.47
23.3 [c]	0.20	12.50	1.64	0.73
	0.30	8.34	1.84	0.65
	0.40	6.25	2.24	0.54
	0.50	5.00	2.47	0.49
	0.60	4.17	2.39	0.50
	0.70	3.57	2.38	0.50
	0.80	3.13	2.66	0.45
	0.90	2.78	2.72	0.44

[a] The total reaction volume varied between 20.0 and 21.0 ml. [b] Sample R1. [c] Refers to the homogeneous catalyst (23.3 mg $RuCl_2(PPh_3)_3$ corresponds to 100 mg of sample R2).

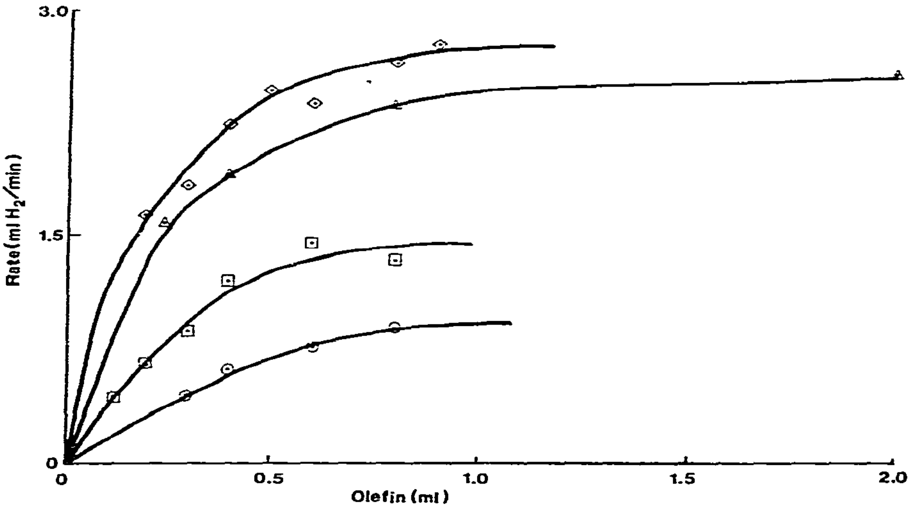

Fig. 4. The rate of hydrogenation of 1-hexene as a function of [Ru] and [olefin]. Data refer to sample R2 (⊙ 100 mg, ⊡ 150 mg, △ 300 mg) or $RuCl_2(PPh_3)_3$ (◇ 23.3 mg).

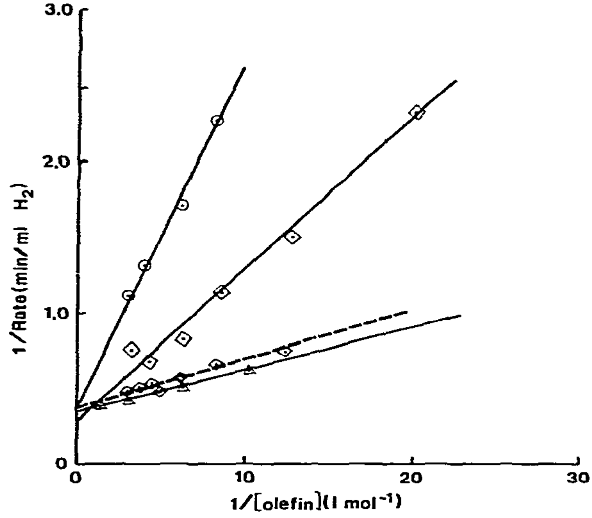

Fig. 5. Plot of 1/[olefin] vs. 1/rate for the hydrogenation of 1-hexene. Data refer to sample R2 (⊙ 100 mg, ⊟ 150 mg, △ 300 mg) or $RuCl_2(PPh_3)_3$ (◈ 23.3 mg).

average maximum rate obtained from our data is 3.0 ± 0.5 ml min^{-1}.

Effect of hydrogen concentration. We have studied the effect of the variation of $[H_2]$ by two methods: (1) variation of the stirring rate and (2) variation of H_2 pressure above the reaction solution and consequently of $[H_2]$ in solution (Table 4). A plot of stirring rate versus reaction rate is shown in Fig. 6. An increase in stirring rate gives a linear increase in the reaction rate above 100 rpm. This effect is due to an increase in the interaction between H_2 and catalyst on agitation of the solution. The effect is small, suggesting that minor changes in the stirring rate will have little effect on the reproducibility of the reaction rate data. Variation of the hydrogen pressure above the reaction solution, and consequently of $[H_2]$ in solution, was achieved by filling the hydrogenation apparatus with mixtures of hydrogen and nitrogen. A plot of hydrogen pressure versus reaction rate (Fig. 7) shows a linear relationship. Both the above effects suggest that under the conditions of our reaction the reaction rate α $[H_2]$.

TABLE 4

EFFECT OF $[H_2]$ ON THE HYDROGENATION RATE [a]

Stirring rate (rpm)	Rate (ml min^{-1})	$p(H_2)$ (atm) [b]	Rate (ml min^{-1})
0	0.08	0.45	0.63
100	0.71	0.56	0.75
300	0.92	0.82	1.03
500	1.03		
700	1.23		

[a] Hydrogenation of 0.16 *M* 1-hexene with sample R3 (100 mg). [b] Hydrogenation carried out under a N_2/H_2 mixture; total pressure of 0.82 atm.

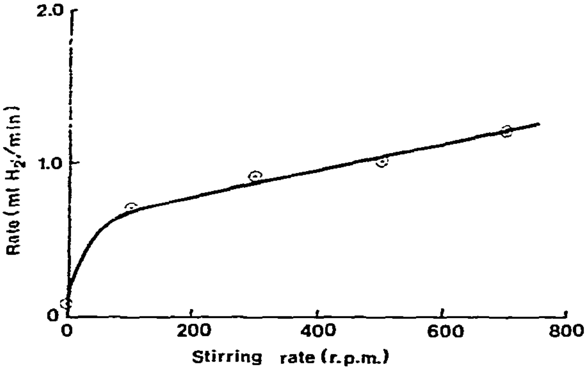

Fig. 6. Effect of stirring rate on the hydrogenation of 1-hexene (sample R3).

Effect of ruthenium concentration. A consideration of the data in Table 3 indicates that at high [olefin] the reaction rate $\propto$ [Ru]. This is shown in Fig. 8.

A plausible mechanism which has been proposed by James [9], for the homogeneous catalytic hydrogenation of an olefin is:

$$\begin{aligned}
&\mathrm{RuClHP_3} && \overset{K_1}{\rightleftharpoons} && \mathrm{RuClHP_2 + P}\\
&\mathrm{RuClHP_2 + olefin} && \overset{K_2}{\rightleftharpoons} && \mathrm{RuCiHP_2(olefin)}\\
&\mathrm{RuClHP_2(olefin)} && \overset{K_3}{\rightleftharpoons} && \mathrm{RuClP_2(alkyl)}\\
&\mathrm{RuClP_2(alkyl) + P} && \overset{K_4}{\rightleftharpoons} && \mathrm{RuClP_3(alkyl)}\\
&\mathrm{RuClP_3(alkyl) + H_2} && \overset{k}{\rightarrow} && \mathrm{RuClHP_3 + alkane} \qquad (\mathrm{P = PPh_3})
\end{aligned}$$

If the total amount of ruthenium in solution, $[\mathrm{Ru}]_{\mathrm{total}}$ is in the form $\mathrm{RuClHP_3}$ and $\mathrm{RuClP_3(alkyl)}$, then the rate law becomes

$$\mathrm{Rate} = \frac{kk'[\mathrm{Ru}]_{\mathrm{total}}[\mathrm{olefin}][\mathrm{H_2}]}{1 + k'[\mathrm{olefin}]}\,, \qquad (k' = K_1K_2K_3K_4)$$

This equation has the same form as that derived by Wilkinson et al. [5]. Our kinetic data for the polymer supported catalytic reaction are thus in accord with this general form of the rate law i.e. rate $\propto$ [$\mathrm{H_2}$], [Ru] and [olefin]/(1 + [olefin]), under our experimental conditions. This suggests that the mechanism of olefin hydrogenation could be the same for both the homogeneous and polymer supported catalytic reactions.

A major problem encountered in the area of polymer supported catalysis is that of elution of catalyst from the polymer during a reaction [20]. In our initial experiments we prepared the catalysts as outlined in the Experimental section and extracted the polymer in a soxhlet apparatus with benzene. On per-

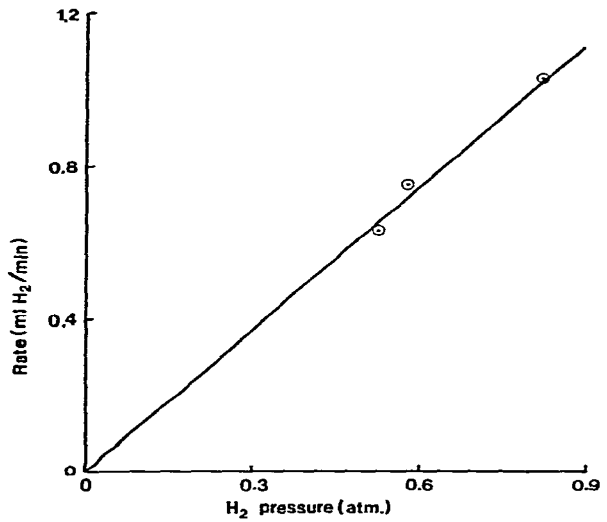

Fig. 7. Effect of hydrogen partial pressure on the hydrogenation of 1-hexene (sample R3).

forming our hydrogenation reactions elution of catalysts into the reaction solvent could readily be detected. However, by changing our extraction solvent to the reaction solvent (1/1 benzene/ethanol) this problem was avoided. Thus no catalyst elution could be detected in the solvent system at the end of a hydrogenation reaction, either visually or by using a UV-visible spectrophotometer. Even after allowing the solution to stand for several days no catalyst could be detected in solution.

Deactivation of a catalyst dissolved in a solvent over a period of time is a common problem encountered in homogeneous catalysis. Previous work has

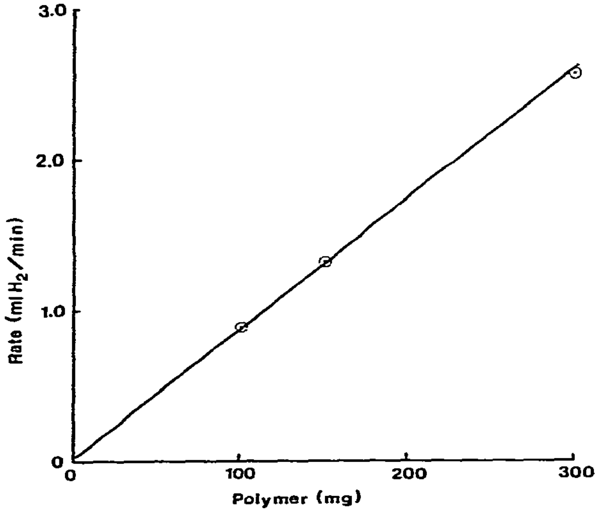

Fig. 8. Effect of [Ru] on the hydrogenation of 1-hexene (sample R2).

suggested that the use of polymer support reagents could help to overcome this problem [21]. We thus investigated this problem for our polymer supported system. Repetitive hydrogenation reactions recorded on the same catalyst indicates a slow decrease in rate with each successive run. This is presumed to be due to adventitious addition of oxygen to the reaction system. However, it is also apparent that the catalyst could decompose on standing in solution as the reaction rate falls to ~10% of its original value if the catalyst is allowed to stand under hydrogen for a period of 6 days (Table 5). The residual rate could be due to the presence of ruthenium metal, a known hydrogenation catalyst [22].

We have also attempted to determine the effect of storage on a used, dried, catalyst sample. Thus, after an hydrogenation reaction was performed, solvent was removed in vacuo, and the polymer stored for 2 months. The catalyst was then used for a repeat hydrogenation reaction. At this stage the polymer had changed from dark brown to green and the reaction rate had fallen to 50% of its original value. This result suggests that the catalyst IV, can indeed be stored in the solid state but that stringent conditions to exclude oxygen must be observed if catalyst deactivation is to be avoided. The susceptibility of the catalyst to facile oxygen deactivation strongly suggests that it is the ruthenium-hydride complex, IV. Further, the oxidized complex is green which is the same colour as the complex obtained by oxygen deactivation of $RuClH(PPh_3)_3$.

To explore facets of the catalytic reaction which will be specifically affected by the presence of the polymer support, we have investigated the effect of olefin chain length, olefin "bulkiness", solvent and metal loading on the hydrogenation reaction. Different rates of hydrogenation have been observed with olefins of varying chain length (low metal loadings, vide infra) such that an increase in the chain length results in a decrease in reaction rate (Table 6, Fig. 9). We have also found that the hydrogenation rate is affected by the bulkiness of the olefin. Thus, as the size of the group attached to the terminal olefin is increased (from 1-hexene through styrene to eugenol, Table 6) the hydrogenation rate decreases [23,24]. (When more than one of the hydrogen atoms on the olefin is substituted, e.g. by alkyl groups, minimal hydrogenation is observed with both the homogeneous [4] and polymer supported catalyst.)

The above steric effects arise from the interaction of the olefin with the Ru catalyst in the polymer bead and the steric effects (and reaction rates) are thus

TABLE 5

STABILITY OF CATALYST IN SOLUTION [a]

Polymer in solution (days)	Reaction rate (ml min^{-1})
0	1.81
0.1	1.79
0.2	1.61
1	0.90
4	0.21
6	0.23

[a] Reaction conditions: 300 mg catalyst R3, 0.1 ml 1-hexene per experiment.

TABLE 6

EFFECT OF OLEFIN CHAIN LENGTH AND SIZE ON THE HYDROGENATION REACTION [a]

Olefin	No. of C atoms	Rate (ml min^{-1}) [b]
1-hexene	6	1.63
1-octene	8	1.49
1-decene	10	1.26
1-dodecene	12	1.21
1-hexadecene	16	1.03
1-octadecene	18	0.95
1-hexene [c]		1.23
styrene [c]		0.61
eugenol [c]		0.44

[a] Reaction conditions (unles otherwise stated): sample R1 250 mg; olefin, 4.80 mmol; solvent, 1/1 benzene/ethanol; NEt_3, 0.20 ml; total reaction volume, 20 ml. [b] Under identical reaction conditions but using $RuCl_2(PPh_3)_3$ (16.0 mg) the hydrogenation rate for all the linear olefins was the same (1.1 ml min^{-1}). [c] Sample R5, 250 mg. Hydrogenation rates were all 1.1 ml min^{-1} when $TuCl_2(PPh_3)_3$ was used to catalyse the reactions.

influenced by both the reaction solvent and the metal loading within the polymer. The effect of solvent is revealed by our studies on the ratio of the rates of hydrogenation of styrene/1-hexene in ethanol-benzene mixtures of varying composition (Fig. 10) (see also our earlier discussion on the choice of reaction solvent). As the % benzene in the solvent mixture increases the polymer swells and the ratio tends to unity i.e. both small and large olefins can now penetrate the bead pores with ease. At lower benzene compositions the polymer shrinks and it now becomes more difficult for the larger olefins to enter the bead pores and be hydrogenated [18,23]. Consequently, the rate ratio now tends to zero. Also, as small volumes of olefin were used (0.30—1.00 ml), effects due to a change in solvent polarity can be neglected [4]. The second factor which influ-

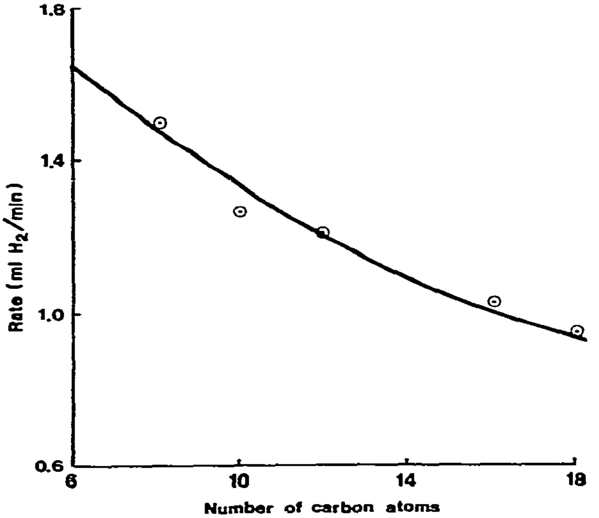

Fig. 9. Effect of olefin chain length on the hydrogenation rate (sample R1).

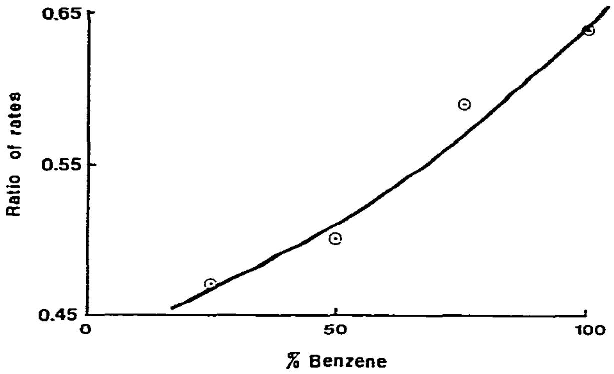

Fig. 10. The ratio of the hydrogenation rate of styrene/1-hexene as a function of % benzene in the solvent mixture.

ences the hydrogenation rate is metal loading (i.e. % Ru) on the polymer. Since all our polymer supported reagents contain a P/Ru ratio of ~3/1 the effect of phosphine loading on the reaction rate can be ignored [25,26]. The effect of metal loading is revealed by the following studies:

1. Use of III for the hydrogenation of 1-hexene indicates that when equal amounts of polymer supported reagents R1 and R2 (Table 7) are used the rate remains approximately equal even though the absolute amount of Ru used is greater in R2. Similarly, with the larger beads (R4, R5) an actual decrease in hydrogenation rate is observed for equal amounts of polymer, even though the amount of Ru has again increased. We interpret this result as implying that at high metal loadings not all the Ru will be used to hydrogenate the olefin i.e. the effective surface area of Ru decreases as the metal loading increases.

2. We have also investigated the styrene/1-hexene hydrogenation rate ratio as a function of Ru loading on the polymer. Fig. 11 indicates that a linear rela-

TABLE 7

EFFECT OF METAL LOADING ON THE HYDROGENATION OF OLEFINS [a]

Sample	Polymer (mg)	Ru (mg) [b]	Rate of hydrogenation	
			1-hexene (ml min^{-1})	$\frac{\text{styrene}}{\text{1-hexene}}$
R1	250	1.92	1.63	0.32
	378	2.91	2.59	
R2	150	3.96	1.45	
	250	6.59	1.58	0.46
R3	100	3.26	1.29	
R4	250	6.90	1.66	0.47
R5	250	7.98	1.23	0.50
[c]		1.69	1.10	~1.00
[c]		2.41	2.13	~1.00

[a] Reaction conditions: 0.240 M olefin, 0.20 ml NEt_3. [b] Total amount of Ru used in the reaction.
[c] $RuCl_2(PPh_3)_3$.

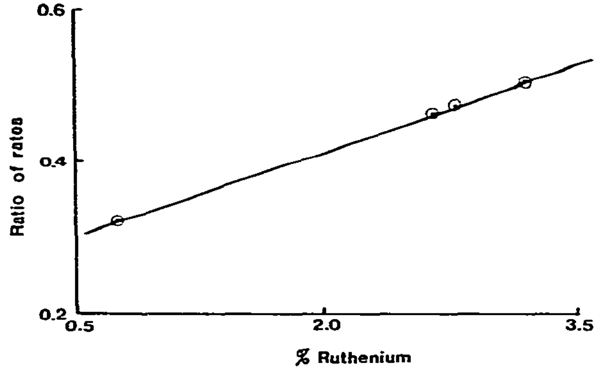

Fig. 11. Ratio of hydrogenation rates as a function of % Ru loaded on the polymer.

tionship is observed between the ratio of the rates and the % Ru loading on a polymer; i.e. the figure represents the rates for equal amounts of Ru but different amounts of polymer. This result we interpret as arising from the decreased ability of the olefin to penetrate the bead (at high loading) before hydrogenation occurs. Consequently, as the Ru loading on a polymer increases the selectivity in olefin hydrogenation decreases.

3. This is further highlighted by the hydrogenation reactions of olefins of varying chain length catalysed by polymers with varying Ru loadings. When a polymer has a low Ru loading (e.g. R1) significant discrimination in the reaction rate, as the olefin chain length is varied, is observed. (Table 6, Fig. 9). However, for polymers containing a higher Ru loading (e.g. R2) less discrimination is observed; for all the olefins listed in Table 6, the hydrogenation rate is ~1.2 ml min^{-1}). At the higher metal loading effectively more Ru is at or near the bead surface and consequently the rates with different olefins will be less influenced by the ability of the olefin to penetrate the bead pores. Further support for this idea is given by the hydrogenation of the olefins by $RuCl_2(PPh_3)_3$ (16.0 mg) which, under our reaction conditions gives a value of ~1.1 ml min^{-1} for all the olefins listed in Table 6 (cf. [4]).

Our results thus indicate that for efficient catalytic activity and high hydrogenation selectivity a low loading of Ru on a polymer support is required. Indeed, it is more advantageous to use large amounts of polymer containing low Ru loadings than small amounts of polymer with a high Ru loading. Our results reveal that the rates at low loadings on the polymer supports approach the rates corresponding to the homogeneous system. Consequently, at high absolute ruthenium concentrations (low loading) the polymer supported catalyst should be superior to the homogeneous catalyst, which has a limited solubility and thus a limiting hydrogenation rate.

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