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KINETIC STUDIES IN VARIOUS MEDIA ON SOME HYDROGENATION REACTIONS CATALYZED BY POLYMER-ANCHORED $RhCl(PPh_3)_3$

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Summary

A study has been made of the hydrogenation of cyclohexene, 1-hexene and styrene at atmospheric pressure catalysed by $RhCl(PPh_3)_3$ supported on styrene-divinylbenzene copolymers with 1%, 2% and 4% cross linking. The dependence of the hydrogenation rate on the concentration of the olefin, the amount of catalyst, and the nature of the solvent was investigated. The hydrogenation rate is lower than for homogeneous catalysis but the dependence of the rate on the examined parameters is similar. The ratio between the rates for 1-hexene and cyclohexene is higher than that in the homogeneous phase. This increase in selectivity may be due to steric hindrance around the active sites of the resin. The solvent effects revealed that the hydrogenation rate also depends on the degree of swelling of the resin.

Introduction

During the past decade, much effort has been devoted to the anchoring of homogeneous catalysts to polymeric supports [1]. Use of such heterogeneous catalysts allows some limitations observed in homogeneous catalysis to be avoided; for example, saturation of the solution at high catalyst concentrations and difficulties in separating and recovering the expensive catalyst. One of the more thoroughly studied anchored catalysts is Wilkinson's catalyst, $RhCl(PPh_3)_3$, attached to a polystyrene-divinylbenzene resin. While much is known about the properties of this catalyst on the preparative scale [2—5], to our knowledge only one paper [6] has dealt with the kinetics and mechanism of the hydrogenation of simple olefins; that paper reports results for the relative rates of hydrogenation of 1-hexene and cyclohexene observed using resin beads of varying mesh, but the data were not always self consistent. The negligible variation in selectivity, observed in changing the solvent, seems surprising in the light of the dependence of the rate on the pore size. We thus decided to reinvestigate the hydrogenation kinetics of simple olefins, including a study of the effect of the substrate concentration on the rate. Resins with different degrees of cross-linking were also examined in order to get better insight into the effect of solvents.

Experimental

Materials

Styrene-divinylbenzene copolymers were commercially available products; those with 1% and 4% divinylbenzene (200—400 mesh) were obtained from Poly-Sep, that with 2% from Fluka. The $RhCl(PPh_3)_3$, butyllithium and *NN,N'N'* tetramethylenediamine (TMEDA) were also commercial products. All solvents were distilled, dried, and degassed by standard procedures. The olefins were distilled under nitrogen before the reactions.

Preparation of anchored catalyst

All manipulations were performed under nitrogen. Of the various methods [7,8,9] proposed for polymer functionalization, that suggested by Grubbs [8] gave the best results. In a typical reaction, butyllithium (1.6 *M* in hexane) (80 ml) complexed with TMEDA (20 ml) was slowly added to a stirred suspension of 10 g resin in 400 ml cyclohexane, and the mixture was refluxed for 5 h. The red-brown, lithiated resin was filtered off, washed with n-pentane, and suspended in 50 ml of tetrahydrofuran; 20 ml of chlorodiphenylphosphine were added, and the mixture was stirred for 24 h. The phosphinated resin so obtained was washed successively with 1 : 1 water-acetone, benzene and methanol and dried under vacuum. The phosphorus content of the resin was determined spectrophotometrically as PO_4^{3-} obtained by decomposition with HNO_3-H_2SO_4 and subsequent oxidation with $HClO_4$.

The anchoring of $RhCl(PPh_3)_3$ was performed by Pittman's method [5]; equimolar Rh/P ratios were always used. Table 1 lists the Rh and P contents of the catalysts; these were determined by Alfred Bernhardt Analytische Laboratorien, Gummersbach, West Germany.

The kinetic runs were carried out at constant atmospheric pressure in an apparatus similar to that previously described [10]. A known amount of solvent was placed in the reaction flask and H_2 was passed through for 30 minutes. The appropriate amount of catalyst was added, and the system equilibrated again by passage of H_2 for 30 minutes. The weighed sample of olefin was added, and the hydrogen uptake was monitored. The total volume of the liquid phase was 12 ml in all cases.

Kinetic data were obtained up to an absorption of 25 ml H_2 (measured in our work conditions), corresponding to about 10% consumption of the olefin in most cases. Under the conditions used the H_2 concentration was constant, and the olefin concentration approximately constant. A constant rate of hydrogen uptake was expected and was generally found. The rates reported for each run are therefore averages of the values observed in successive time intervals; the standard deviation of the measured values was usually less than 10%. The uncertainties reported in Table 4 are standard deviations estimated by assuming the various kinetic runs to be independent. A study of the homogeneous hydrogenation of cyclohexene in benzene solution catalyzed by the Rh complex in our apparatus gave results similar to Wilkinson's.

Results and discussion

The data in Table 1 indicate that the P/Rh molar ratio in the resins used was always less than 3; since the presence of free $-PPh_2$ groups is very likely, this strongly suggests that a substantial amount of the Rh complex has suffered some structural modification, possibly involving formation of dimeric structures as suggested by Reed et al. [11,12]. The Table also shows that Rh and P leaching occurs during the hydrogenations; the observed ratio between the lost P and Rh in g-atoms, viz. 1.7, is intermediate between that expected for the loss of a monoanchored dimeric species (1.5) and that for the loss of a monoanchored monomeric species (2.0).

Table 2 and Fig. 1 show the effects of varying the cyclohexene concentration with a given catalyst R_1. It is apparent that the rate increases with increasing olefin concentration up to a limiting value at high substrate concentrations. A plot (Fig. 2) of the reciprocal of the hydrogenation rate vs the reciprocal of the substrate concentration is linear. This indicates that the rate equation is of the form:

$$v = \frac{K\,[\text{olefin}]}{A + B\,[\text{olefin}]}$$

Extrapolation to 1/[olefin] = 0 in the plot of Fig. 2 gives a value of 1.75 ml/min for the maximum hydrogenation rate under our conditions.

Comparison with Wilkinson's data for the homogeneous catalysis shows that his limiting value of the rate is about four times higher for a Rh content one tenth of that we employed. However, the ratio between the reaction rates in homogeneous and heterogeneous phases is strongly dependent on the amount of catalyst present. For example, under our usual conditions, with a Rh content equal to that employed by Wilkinson the heterogeneous catalyzed hydrogenation is about one tenth as fast as the homogeneous process.

The hydrogenation rate depends also on the amount of catalyst present (see Table 3). As shown in Fig. 3, a linear correlation exists between the rate and the amount of catalyst; the plot does not pass through the origin, the intercept being higher for 1-hexene. The reason for this is not clear; the same phenomenon was observed by Wilkinson, but the explanation he proposed, i.e. the for-

TABLE 1

Rh AND P CONTENTS OF RESINS

Catalyst [a]	Rh (%)	P (%)	P : Rh molar ratio
R_1	8.06	5.70	2.35
R_1 [b]	6.15	4.71	2.54
R_2	8.52	5.85	2.28
R_4	6.62	4.81	2.41

[a] Subscripts 1, 2 and 4 indicate the degree of cross linking of the resins. [b] Recycled catalyst

TABLE 2

HYDROGENATION RATES FOR VARIOUS CONCENTRATIONS OF CYCLOHEXENE IN BENZENE, WITH A FIXED AMOUNT OF R_1 (0.2 g) [a].

[cyclohexene] (*M*)	Rate (ml H_2 absorbed/min)			
0.082	0.32			
0.25	0.74	0.62		
0.41	0.98	1.04		
0.82	1.13	1.26	1.17	1.00
1.23	1.23	1.51	1.44	

[a] V_{tot} = 12 ml; P = 1 atm.; T = 25°C.

mation of catalytically inactive dimeric forms at high complex concentration cannot be applied to the heterogeneous system. The evidence indicates that the dependence of the rate on the examined parameters in heterogeneous catalysis is similar to that for the homogeneous process, pointing to a similar reaction mechanism in both situations. However, different catalytic reaction kinetics, whether homogeneous or heterogeneous, frequently conform to similar kinetic equations, the existence of a limiting rate being due to saturation of the active sites at sufficiently high substrate concentrations. On the basis of the available data we cannot discriminate between these two possibilities.

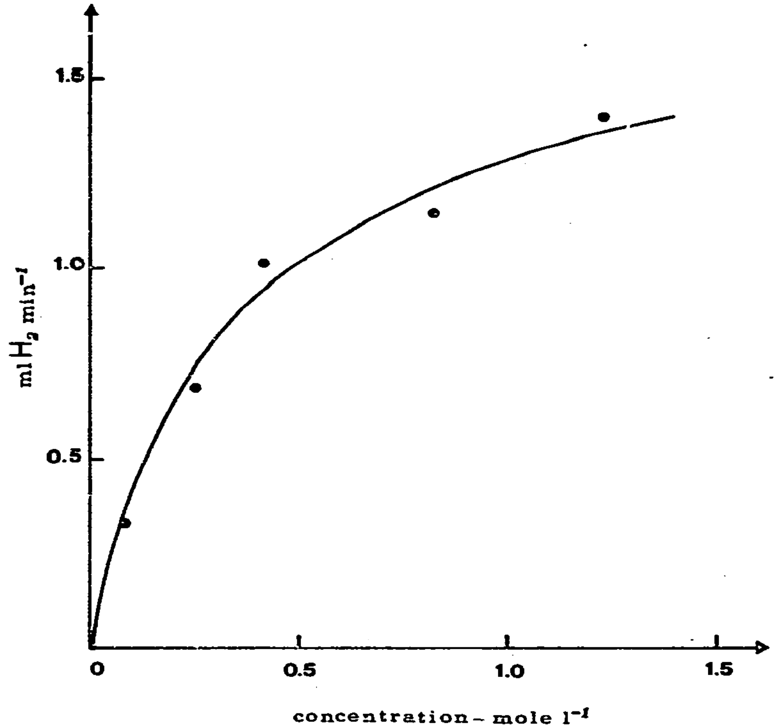

Fig. 1. Plot of the rate of hydrogenation of cyclohexene (ml H_2 absorbed/min) vs olefin concentration, in benzene at 25°C with 0.2 g R_1.

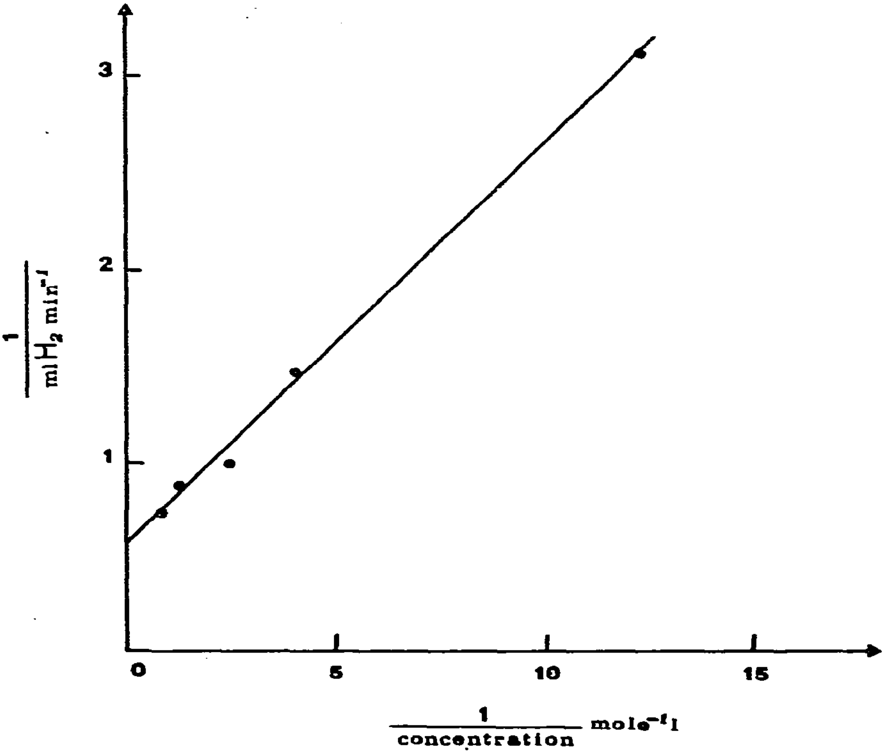

Fig. 2. Plot of the reciprocal of the rate of hydrogenation of cyclohexene (ml H_2 absorbed/min) vs the reciprocal of the olefin concentration, in benzene at 25°C with 0.2 g R_1.

Table 3 reports kinetic data for the hydrogenation of 1-hexene. In this case, including runs involving R_2 and R_4 (see Table 4), the hydrogen absorption rate is about twice that of cyclohexene; this ratio is to be compared with values of 2.55, 0.81 and 1.25 reported by Grubbs for resins with 2% cross linking [4]. From literature data for the homogeneous phase it can be estimated [6,13] that the difference between the hydrogenation rates of these two olefins is not greater than 40%. This points to a higher selectivity of the heterogeneous compared with the homogeneous catalyst. As already suggested, the explana-

TABLE 3

HYDROGENATION RATES FOR CYCLOHEXENE AND 1-HEXENE 0.82 M IN BENZENE AS A FUNCTION OF THE AMOUNT OF CATALYST R_1 [a]

Amount R_1 (g)	Hydrogenation rate (ml H_2 absorbed/min)							
	[cyclohexene] = 0.82				[1-hexene] = 0.82			
0.025	0.32	0.31	0.28		0.61	0.57		
0.05	0.34	0.36	0.46		1.18	1.05	0.93	
0.10	0.65	0.66			0.89	1.19	1.05	1.14
0.20	1.13	1.26	1.17	1.00	1.73	2.26		

[a] V_{tot} = 12 ml; P = 1 atm.; T = 25°C.

TABLE 4

HYDROGENATION RATES IN VARIOUS SOLVENTS USING A FIXED CONCENTRATION (0.82 *M*) OF CYCLOHEXENE OR 1-HEXENE AND A FIXED AMOUNT OF CATALYST [a]

Catalyst Temp. (°C)	Solvent	Hydrogenation rate (ml H_2 absorbed/min)										
		[cyclohexene] = 0.82					average	[1-hexene] = 0.82				average
0.2 g R_1	EtOH	0.22	0.20				0.21 ± 0.01	1.37	1.47	1.46		1.43 ± 0.06
25	Benzene + EtOH (1 : 1)	0.52					0.52	1.70	1.97			1.84 ± 0.19
	Benzene	1.13	1.26	1.17	1.00		1.14 ± 0.11	1.73	2.26			2.00 ± 0.37
0.1 g R_2	EtOH	0.80	0.46	0.53			0.60 ± 0.18	3.29				3.29
40	Benzene + EtOH (1 : 1)	0.72	1.04	1.14			0.97 ± 0.37	2.11	2.38	2.69	2.48	2.42 ± 0.24
	Benzene	1.13	1.03	1.35	1.44	0.94	1.18 ± 0.21	2.32				2.32
0.1 g R_4	EtOH	0.87	0.86				0.87 ± 0.01	4.49	4.38			4.44 ± 0.08
40	Benzene + EtOH (1 : 1)	1.13	1.38				1.26 ± 0.18	2.93	3.26	3.41		3.20 ± 0.25
	Benzene	1.29	1.63				1.46 ± 0.24	2.46	2.46	2.46		2.46

[a] $V_{tot} = 12$ ml; $P = 1$ atm.

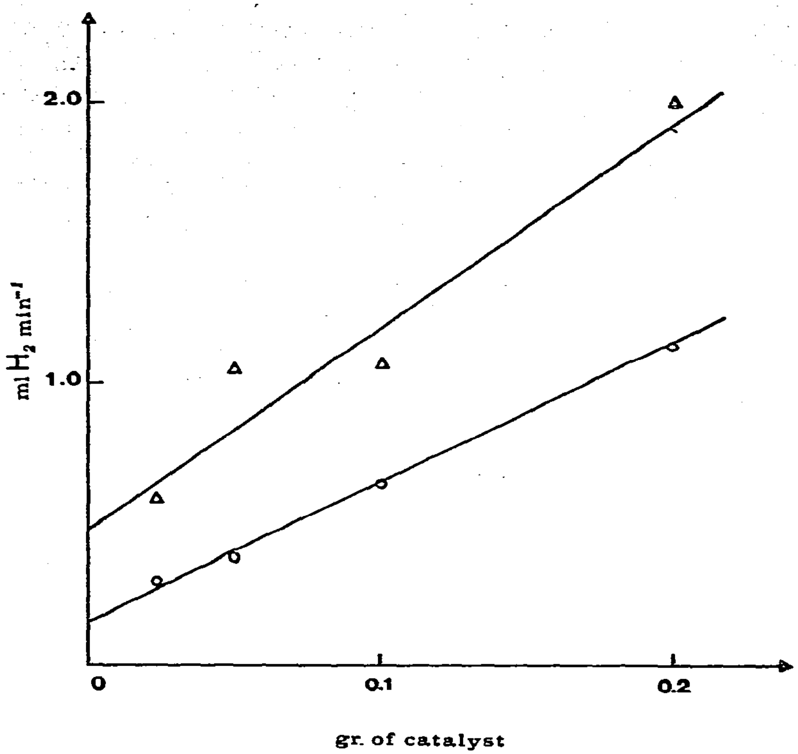

Fig. 3. Dependence of the rates of hydrogenation of cyclohexene (○) and 1-hexene (△) (0.82 *M*) (ml H_2 absorbed/min) on the amount (g) of R_1 at 25°C.

tion might lie in the increased steric hindrance around the catalytically active sites of the heterogeneous catalyst, which will favour the smaller olefin.

The difference between the homogeneous and heterogeneous systems is even more evident when the reactions are carried out in various solvents. Table 4 gives the results for variations in the medium, the catalyst and the substrate. Our first observation was that catalyst R_1 is markedly more active than R_2 and R_4, while these have comparable activities *. This cannot be explained either by the small variations in the Rh or P contents (or in the P/Rh molar ratios) or by the different degree of cross linking of the resins. The reason for this difference in behaviour is not clear; following the suggestion by Reed et al. [12], it can be tentatively ascribed to a varying degree of structural modification of the complex induced by resins with different degrees of cross linking.

In considering the kinetic data obtained on varying the solvent, the olefinic substrate and the degree of cross linking of the copolymer, the following factors must be taken into account: (a) In the homogeneous system the rate of hydrogenation of cyclohexene is more than doubled on going from benzene to 1 : 1 benzene-EtOH as solvent [13]; we obtained a similar result for hydrogenation of 1-hexene. In the heterogeneous system, therefore, the slowest reaction

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* Because of this, reactions with R_2 and R_4 were carried out at 40°C. Experiments at 40°C with R_1 showed behaviour analogous to that at 25°C. For example, for 0.82 *M* 1-hexene the average rates (ml H_2 absorbed/min) were: 3.86 in EtOH; 4.07 in EtOH + benzene (1 : 1); 5.47 in benzene.

would occur in benzene if the solvent effect alone were determining the hydrogenation rate (b) The degree of swelling of a resin depends on the solvent (in our case, the swelling would be greater in benzene than ethanol) and on the extent of cross linking; the greater the cross linking the lower the swelling for a given solvent (c) The hindrance at the double bond varies with the olefin used. Effects (a) and (b) act in opposite directions. Thus ethanol should increase the rate compared with that in benzene because of its greater polarity, while its poorer swelling ability will give rise to more hindrance to access of the bulkiest olefins to the catalytically active sites, so lowering the rate. The rates for hydrogenation of cyclohexene, the most sterically hindered substrate, decrease on going from benzene to ethanol, with all three catalysts; the influence of the degree of cross linking of the resin on the extent of swelling is revealed by the variation of the ratio (*r*) between the hydrogenation rates in ethanol and benzene, which increases from 0.18 for R_1 to 0.60 for R_4. This is in agreement with greater sensitivity of the resin with the lowest degree of cross linking to the swelling ability of the solvent.

The rate for 1-hexene, which is less hindered than cyclohexene, should be less dependent on the swelling. Consistently, with this substrate, *r* is 0.72 for R_1. Moreover, the fact that *r* becomes greater than 1 for R_2 and R_4 (1.42 and 1.80 respectively) indicates that with less swellable resins the influence of the polarity of the solvent (see point (a) above) predominates for the less hindered olefins. However, due to the effect noted under point (b), the rate increase is less than in the homogeneous system. Fig. 4 summarizes the results for the rates of hydrogenation of cyclohexene and 1-hexene in the various media relative to that of cyclohexene in benzene. The solvent effects observed disagree with those observed by Grubbs [6]. Thus, he reported for both substrates a greater increase in the hydrogenation rate on going from benzene to benzene—EtOH (1 : 1) than was found in homogeneous phase. This remarkable rate increase was ascribed by Grubbs to an increase in the substrate concentration inside the resin beads due to a polarity gradient at the solid—liquid interphase. Our data were obtained at a substrate concentration in the range, where it has a small effect on the rate; this might have prevented observation of effects similar to those reported by Grubbs. Thus, we performed some experiments with lower substrate concentrations, and the results are shown in Table 5; the *r* ratios obtained, viz. 0.59 for cyclohexene and 1.14 for 1-hexene, are very similar to those previously found, and so no effect attributable to a concentration increase inside the resin beads is apparent.

In the light of the above discussion, a solvent with good swelling ability and high polarity would be expected to lead to a faster hydrogenation. Tetrahydrofuran meets both requirements (solubility parameter similar to that of benzene [14], and dipole moment [15] 1.7 D), and the rate of hydrogenation of cyclohexene was, indeed, found to be higher in 1 : 1 benzene—THF and pure THF than in benzene; the rates relative to those in pure benzene are 1.66 and 3.26, respectively, for runs with catalyst R_2.

Hydrogenation reactions in various solvents were also carried out using styrene as substrate and R_1 as catalyst. The results listed in Table 6, are similar to those previously discussed, indicating that the same factors again operate and to about the same extent.

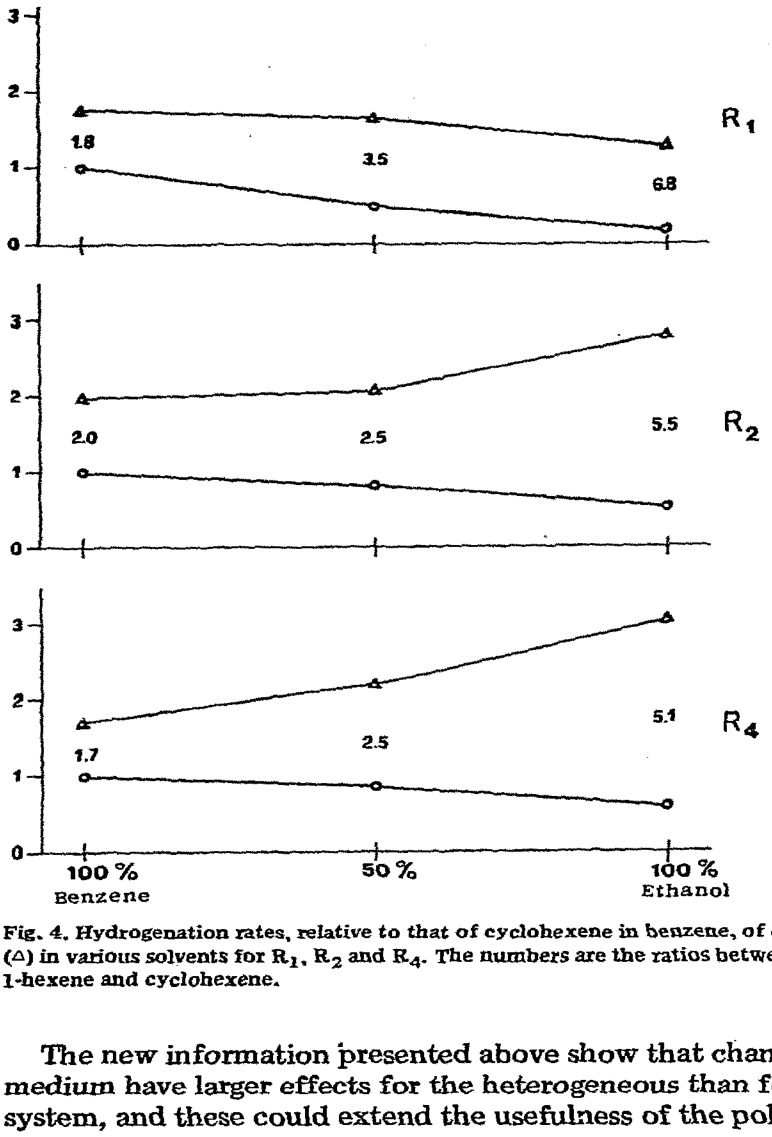

Fig. 4. Hydrogenation rates, relative to that of cyclohexene in benzene, of cyclohexene (○) and 1-hexene (△) in various solvents for R_1, R_2 and R_4. The numbers are the ratios between the hydrogenation rates of 1-hexene and cyclohexene.

The new information presented above show that changes in the reaction medium have larger effects for the heterogeneous than for the homogeneous system, and these could extend the usefulness of the polymer-bound catalysts. In particular, the selectivity of the catalyst can be strongly enhanced by choice of a suitable solvent.

TABLE 5

HYDROGENATION RATES IN BENZENE AND ETHANOL USING A FIXED CONCENTRATION (0.082 *M*) OF CYCLOHEXENE AND 1-HEXENE AND A FIXED AMOUNT OF R_2 (0.1 g)[a]

Solvent	Hydrogenation rate (ml H_2 absorbed/min)							
	[cyclohexene] = 0.082 *M*				average	[1-hexene] = 0.082 *M*		average
EtOH	0.32	0.33			0.33 ± 0.01	1.01	1.04	1.03 ± 0.02
Benzene	0.66	0.50	0.57	0.52	0.56 ± 0.07	1.10	0.69	0.90 ± 0.29

[a] $V_{tot} = 12$ ml; $P = 1$ atm.; $T = 40°C$.

TABLE 6

HYDROGENATION RATES OF STYRENE 0.82 *M* IN VARIOUS SOLVENTS USING A FIXED AMOUNT OF R_1 (0.2 g) [a]

Solvent	Hydrogenation rate (ml H_2 absorbed/min)			
EtOH	1.06	1.10	1.10	
Benzene + EtOH (1 : 1)	2.38	2.13	2.06	
Benzene	2.15	2.04	1.77	2.30

[a] V_{tot} = 12 ml; P = 1 atm.; T = 25°C.

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