Zeolite-Encapsulated Rhodium Catalysts – The Best of Both Worlds?

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The syntheses and catalytic behaviour of rhodium catalysts encapsulated in zeolites are reported. Several parameters are investigated in this catalyst system, including the auxiliary ligands and the zeolite supports used. It is demonstrated that the zeolite support can be crucial in determining the types of products formed from catalytic hydroformylation reactions. The results are rationalised in terms of fundamental principles of organometallic chemistry. This enhances the understanding of these catalyst systems at a molecular level and demonstrates that a synergy exists between the development of new, efficient catalyst systems and understanding chemistry at a fundamental level.

Many organometallic complexes are used successfully in homogeneous catalysis, and as catalysts they are highly selective and operate under relatively mild reaction conditions. However, the benefits of homogeneous catalysts can be compromised by a difficult separation of catalyst from reaction products, or deactivation due to irreversible structural changes. In an attempt to combine the advantages of homogeneous (selectivity, mild reaction conditions) and heterogeneous (facilitated catalyst recovery) systems, molecular/organometallic catalysts have been supported on various metal oxides and organic polymer supports. However, the catalyst has often become detached from the support, and selectivities have been disappointing.

In contrast to the commonly used classical amorphous catalyst supports, such as metal oxides, the crystalline pore structures of zeolites offer a unique potential to improve selectivities, by diffusion phenomena, and to modify catalytic transition states. A further advantage of these catalyst systems is their potential to eliminate the undesirable condensation reactions of the reaction products, which yield heavier products. Condensation products are often environmentally harmful and they decrease product yields. The confined space of a zeolite cavity should prevent condensation reactions from taking place.

The hydroformylation of alkenes to produce aldehydes and/or alcohols, see Equation (i) is one of the most versatile methods for the functionalisation of C=C bonds. It is the largest volume industrial process to make use of a homogeneous catalyst.

$$RCH=CH_2 + CO/H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CHO$$
$$+ RCH_2CH_2CH_2OH \qquad (i)$$
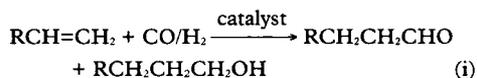
Hydroformylation catalysts typically include a transition metal (M) which enables the formation of metal carbonyl hydride species. These complexes can be modified by additional ligands (L).

The hydroformylation reaction was discovered in 1938 when it was observed that alcohols were present in the product fractions from Fischer-Tropsch reactions over heterogeneous cobalt catalysts (1). Until the 1970s, after Sir Geoffrey Wilkinson discovered that rhodium complexes could function as active hydroformylation catalysts (2), cobalt-based catalysts (unmodified cobalt carbonyls and phosphine-modified cobalt carbonyls) were still exclusively used as hydroformylation catalysts. These cobalt catalysts are also hydrogenation catalysts: thus they tend to give predominantly alcohols (via hydrogenation of aldehydes) as products. Rhodium catalysts are more selective and efficient: they do not function as hydrogenation catalysts and therefore give aldehydes as products. While aldehydes are
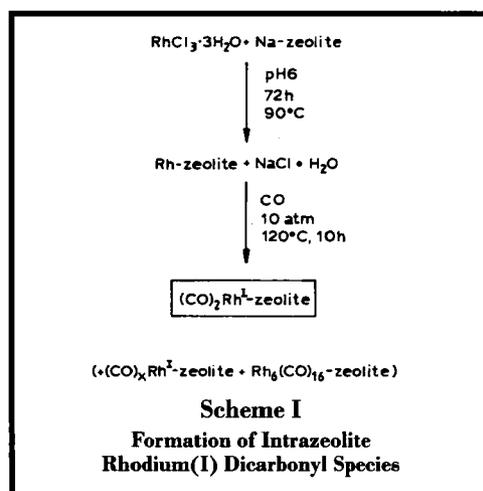
the preferred products if short chain alkenes (< C₄) are used as substrates (the aldehydes are then used for condensation reactions and conversion to phthalate esters for use in PVC synthesis) longer chain products are normally required as alcohols (which can then, for example, be sulfonated for use in the synthesis of biodegradable detergents).

Surprisingly, the range of products from technical hydroformylation has remained nearly unchanged for the past fifteen years (3). From 1965 to 1980 a remarkable diversification of products, refinement of methods and developments of the cobalt-based processes took place, as did the initial penetration and substitution of rhodium-based catalysts in these processes (4). In 1980 less than 10 per cent of all hydroformylation products were produced using rhodium catalysts compared to nearly 80 per cent in 1995. The rapid growth in rhodium-based low-pressure processes was favoured by the milder reaction conditions, simpler (and therefore cheaper) equipment, high efficiency, higher yield of linear products and easier recovery of the catalyst.

Under hydroformylation conditions using [RhH(PEt₃)₃] as a catalyst precursor, it has recently been shown that alkenes give high selectivity to alcohols, rather than aldehydes, if the reaction is carried out in protic solvents, see Equation (ii) (5, 6). Labelling studies show that this unusual selectivity is due to the formation of a hydroxycarbene species (formed via H-bonding to a solvent molecule) which prevents the reductive elimination of the aldehyde species. Metal hydroxycarbene species are those in which the organic moiety containing a hydroxyl group is bonded to the metal centre by a (formal) double bond.

$$RCH{=}CH_2 + CO/H_2 \xrightarrow{\dfrac{[RhH(PEt_3)_3]}{C_2H_5OH}}$$

$$RCH_2CH_2CH_2OH + RCH_2CH(CH_3)CH_2OH \quad (ii)$$
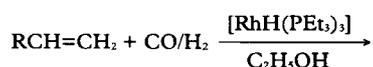
For the production of alcohols, this rhodium-based system should be preferable to a cobalt-containing system as it can operate under milder conditions (120°C, 40 bar compared with

RhCl₃·3H₂O + Na-zeolite

↓ pH6
72h
90°C

Rh-zeolite + NaCl + H₂O

↓ CO
10 atm
120°C, 10h

[(CO)₂Rhᴵ-zeolite]

(+(CO)ₓRhᴵ-zeolite + Rh₆(CO)₁₆-zeolite)

Scheme I
**Formation of Intrazeolite
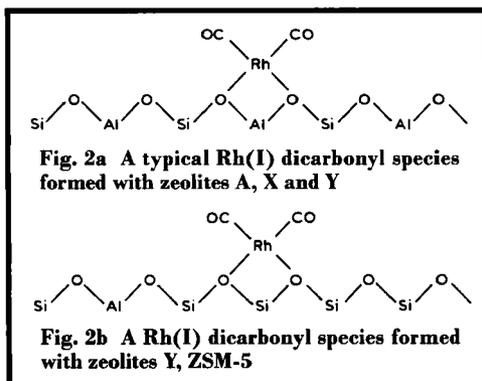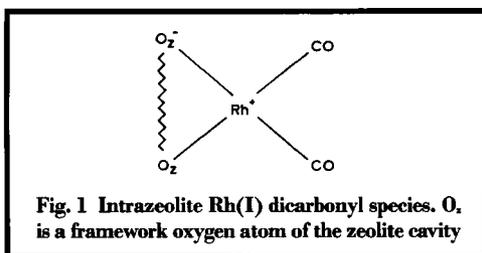Rhodium(I) Dicarbonyl Species**

200°C, 300 bar for cobalt) and it gives the alcohol in **one** step (compared to two steps for cobalt). However, the regioselectivity (the linear:branched or *n:iso* ratio) is rather low, ranging from 1.3 to 2.5, depending on the substrate employed. Thus, we are interested in investigating liquid-phase zeolite-encapsulated systems with a view both to improving catalyst recovery and to determine whether the zeolite cavities will exert any steric restrictions on the reaction, thereby increasing the selectivity.

Although reports have appeared on the use of zeolite-encapsulated rhodium species as liquid-phase hydroformylation catalysts (7, 8), these studies involved different catalyst precursors and reaction conditions to ours, and only resulted in aldehyde formation. Some improvement in selectivity over similar homogeneous systems was observed, but zeolite Y was the only zeolite subjected to detailed study.

Generation of the Catalytic Species

For our studies, the catalysts were prepared by ion-exchange of sodium of zeolites A, X, Y, Y⁴ (zeolite Y with Si:Al = 4) and ZSM-5 for rhodium, see Scheme I, followed by carbonylation of the rhodium-exchanged species. This mainly resulted in the formation of zeolite-encapsulated rhodium(I) geminal dicarbonyl species, see Figure 1 and as represented in Table I. Thus, two framework oxygen atoms, one bearing a
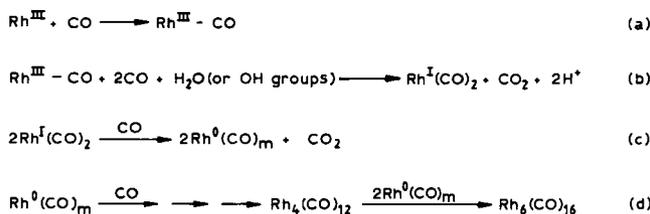
$$O_2^- \diagdown \diagup CO$$
$$Rh^+$$
$$O_2 \diagup \diagdown CO$$

Fig. 1 Intrazeolite Rh(I) dicarbonyl species. O₂ is a framework oxygen atom of the zeolite cavity

$$OC \diagdown \diagup CO$$
$$Rh$$
Si—O—Al—O—Si—O—Al—O—Si—O—Al—O

Fig. 2a A typical Rh(I) dicarbonyl species formed with zeolites A, X and Y

$$OC \diagdown \diagup CO$$
$$Rh$$
Si—O—Al—O—Si—O—Si—O—Si—O—Si—O

Fig. 2b A Rh(I) dicarbonyl species formed with zeolites Y, ZSM-5

negative charge, are co-ordinated to the rhodium(I) ion, thereby completing the expected square-planar co-ordination of a d^8 cation. With zeolite Y, small amounts of the hexanuclear cluster $[Rh_6(CO)_{16}]$ and of another type of rhodium(I) dicarbonyl species were also formed within the zeolite supercage. Similar results were obtained by Rode and colleagues (8) who proposed that the additional rhodium dicarbonyl species was of the form $[Rh^I(CO)_2{}^+O_Z(H_2O)]$; in effect a water molecule has replaced one of the zeolite oxygen atoms in the co-ordination sphere of the rhodium. However, in view of the

fact that water is rigorously excluded from our systems, an alternative explanation is that in zeolites A and X, with a silicon:aluminium ratio of 1, most of the aluminium atoms are separated by only one silicon atom. The rhodium dicarbonyl species thus adopts the form shown in Figure 2a, where it bonds to two zeolite oxygen atoms which are attached to an aluminium atom. Zeolite Y has a silicon:aluminium ratio of 2.5; thus, several of the aluminium atoms are separated by more than one silicon atom. A second, additional $Rh^I(CO)_2$ species could then form in which the rhodium bonds to two zeolite oxygen atoms attached to a silicon atom, as shown in Figure 2b. Presumably, in ZSM-5, with a silicon:aluminium ratio of 100, the predominant species is that shown in Figure 2b.

With zeolite Y^4, $[Rh_6(CO)_{16}]$ was the only intrazeolite species formed. Thus, the sequence of reactions represented in Scheme II could take place during the synthesis of the intrazeolite rhodium species. Zeolites A and X are of relatively low acidity and thus the reaction shown in Scheme II will not proceed to completion (beyond step (b)). Due to the higher acidity of zeolite Y, the oxygen atoms of the zeolite cavities are sufficiently nucleophilic to effect a small degree of cluster formation. The highly acidic zeolite Y^4 will contain oxygen atoms of even higher nucleophilicity, resulting in complete conversion to the cluster. Although zeolite ZSM-5 has even higher acidity, the smaller tunnel dimensions prevent formation of the cluster species.

It is now apparent that the acidity of the

Table I				
Nature of Intrazeolite Species Formed with Various Zeolites				
Zeolite	Si:Al ratio	Pore size, Å	Cavity diameter, Å	Intrazeolite species formed
A	1	4.4	11.4	(CO)₂Rh-A
X	1	7.4	13	(CO)₂Rh-X
Y	2.5	7.4	13	(CO)₂Rh-Y + (CO)ₓRh-Y + Rh₆(CO)₁₆-Y
Y^4	4	7.4	13	Rh₆(CO)₁₆-Y^4
ZSM-5	100	interconnecting tunnels, 5.5 Å		(CO)₂Rh-ZSM-5

$$Rh^{III} + CO \longrightarrow Rh^{III} - CO \qquad (a)$$

$$Rh^{III} - CO + 2CO + H_2O \text{(or OH groups)} \longrightarrow Rh^{I}(CO)_2 + CO_2 + 2H^+ \qquad (b)$$

$$2Rh^{I}(CO)_2 \xrightarrow{CO} 2Rh^{0}(CO)_m + CO_2 \qquad (c)$$

$$Rh^{0}(CO)_m \xrightarrow{CO} \longrightarrow \longrightarrow Rh_4(CO)_{12} \xrightarrow{2Rh^{0}(CO)_m} Rh_6(CO)_{16} \qquad (d)$$

Scheme II
Proposed Formation of Intrazeolite Rhodium Carbonyl Species

zeolite support is crucial in determining the type of intrazeolite species formed. The geminal dicarbonyl species $(CO)_2Rh\text{-}O_z$ were then investigated as hydroformylation catalysts in the presence of various phosphine ligands.

Hydroformylation of 1-Hexene

The results from experiments on the catalytic hydroformylation of 1-hexene are shown in Table II. It is apparent that the zeolite has an effect not only on the nature of the rhodium complex formed within it, but also on the catalytic properties of these species. It was found that:

[a] the regioselectivity (*n:iso* ratio) is higher than that obtained with the analogous homogeneous systems (5, 6);

[b] a higher proportion of linear product is formed with zeolite Y than with zeolite X (in some cases the *n:iso* ratio is doubled for Y compared with X) and

[c] although the regioselectivity is higher with zeolite Y, the activity is generally lower. The chemoselectivity of the reactions is similar to that observed using soluble catalysts prepared in situ from $[Rh_2(O_2CMe)_4]$ and phosphines (5, 6). Thus, if the reactions are carried out in ethanol (EtOH), primary phosphines give C_7 alcohols. This is due to the proton-donating

				Table II				
			Hydroformylation of 1-Hexene Using $(CO)_2Rh$-Zeolite as Catalyst Precursor[a]					
Solvent	Zeolite	Pressure, p, atm	PR_3	Yield of C_7 alcohols, per cent	Ratio *n:iso*	Yield of C_7 aldehydes, per cent	Ratio *n:iso*
Toluene EtOH	X	50	PEt₃	21	3.5	79	3.3
			PPh₃	52	100 % linear	38[b]	2.9
			PEt₃	80	2.5	–	–
			PPr^n_3	32	3.5	–	–
			PPr^i_3	28	3.8	–	–
			PEt₂Ph	40	21	–	–
Toluene EtOH	Y		PEt₃	15	3.9	60	3.8
			PPh₃	36	100 % linear	35[c]	5
			PEt₃	70	5.1	–	–
			PPr^n_3	80	5.3	–	–
			PPr^i_3	72	5.5	–	–
			PEt₂Ph	30	26	–	–
	Y^d		PEt₃	–	–	–	–

[a] Hexene (1 cm³), solvent (4 cm³), 120°C, 17 h, [Rh] = 3.5 × 10⁻³ mol dm⁻³, [PR_3] = 3.5 × 10⁻² mol dm⁻³
[b] Diethyl acetals of C_7 aldehydes are also formed (10 per cent); [c] Diethyl acetals of C_7 aldehydes are also formed (30 per cent)
[d] Catalyst precursor [RhH(PEt₃)₃], zeolite Y added to reaction mixture. Products are exclusively diethyl acetals (100 per cent) of C_7 aldehydes (*n:iso* = 3.1)

Scheme III
Catalytic Cycle for the Hydroformylation of 1-Hexene by
Intrazeolite Rhodium(I) Species (PR₃ = PEt₃; R* = CH₂CH₂CH₂CH₃)
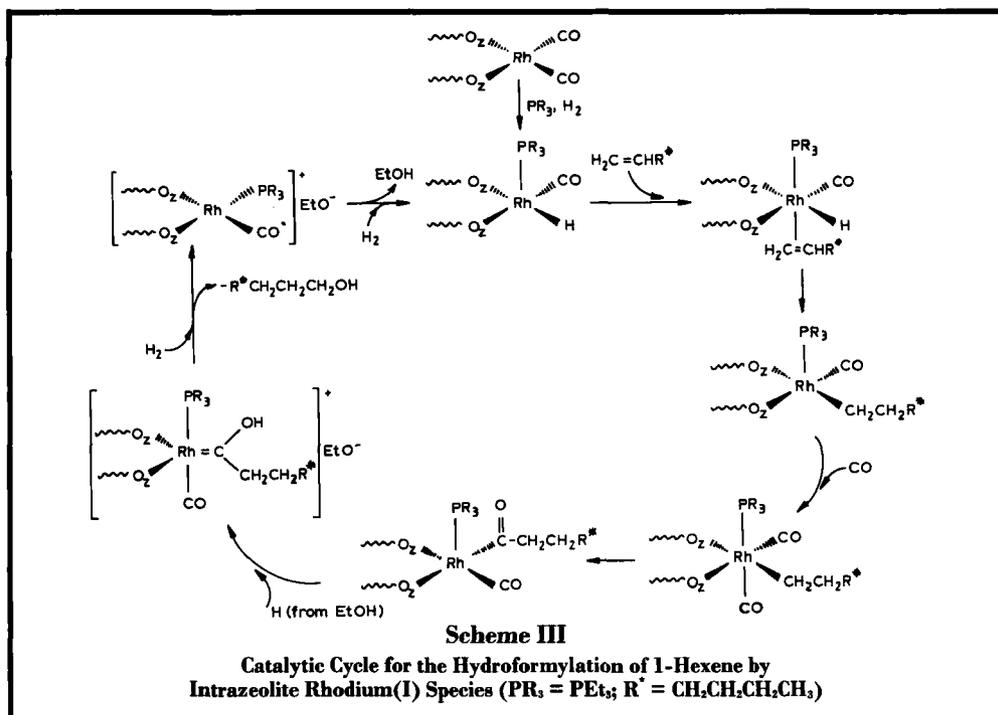
ability of EtOH, facilitated by strongly electron-donating phosphines such as PEt₃, resulting in the formation of hydroxycarbene species from acyl intermediates, as represented in Scheme III and Figure 3.

This has been proven by labelling studies using EtOD in place of EtOH. If toluene is used as a solvent, or if PPh₃ is used in place of more basic alkylphosphines like PEt₃ or PPr''₃, a mixture of C₇ aldehydes and C₇ alcohols is formed. In these cases, the alcohols derive from hydrogenation of the aldehydes with the linear aldehydes being preferentially hydrogenated. This is especially apparent in the case of the PPh₃ system where only linear alcohols are observed. However, the overall selectivity in this case is disappointing; a substantial amount of aldehyde is present (about 35 per cent) together with diethylacetals of the C₇ aldehydes. These comprise 10 per cent of the product mixture for zeolite X, but 30 per cent for zeolite Y. (It was initially thought that the PPh₃ molecule might be too large to migrate through the zeolite channels. However, at elevated temperatures, lattice vibrations in the zeolite may permit the bulky phosphine to pass through.)

Another substantial change in selectivity is obtained upon changing the nature of the phosphine ligand, for instance, the substitution of PEt₃ by the more sterically demanding PEt₂Ph ligand gives dramatic results. By varying the phosphine ligand it is possible to achieve n:iso

Fig. 3 The formation of a hydroxycarbene intermediate

Scheme IV
Hydroformylation of Styrene
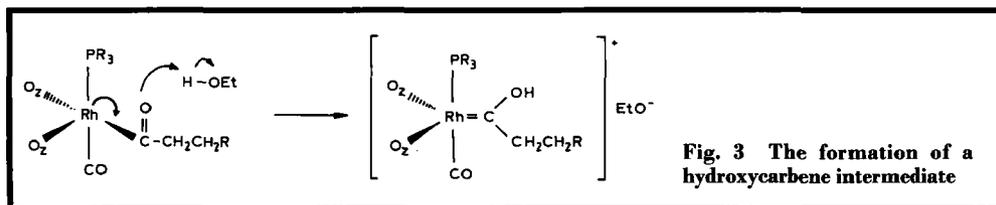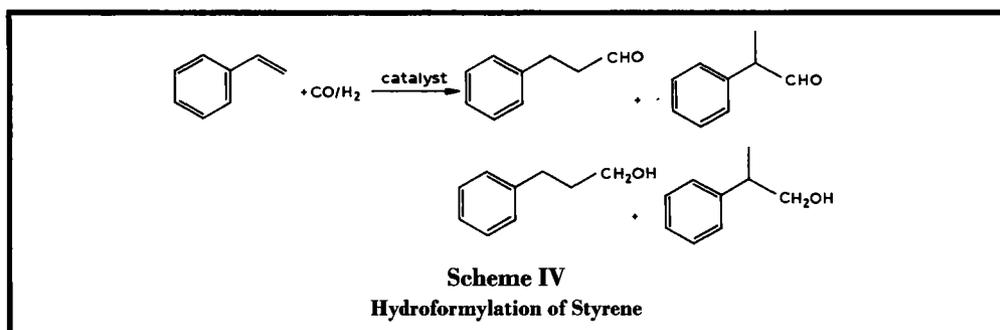
ratios ranging from 2.2:1 to 24:1 (zeolite X) or from 4:1 to 26:1 (zeolite Y) for C_7 alcohols, see Table II. The achievement of an *n:iso* ratio of 26:1 is an exciting result as this catalyst system now has comparable selectivity to Wilkinson's catalyst and represents a greater than 10-fold improvement in selectivity when compared to the analogous homogeneous catalyst system.

Zeolite Y^4, containing the cluster species $[Rh_6(CO)_{16}]$, showed no catalytic activity, while ZSM-5 gave selectivities somewhat lower that zeolites X or Y. This is presumably because ZSM-5 consists of interconnecting tunnels rather than discrete cavities. Zeolite A gave results very similar to the homogeneous systems; indeed, when the solution recovered from the reaction was tested, it exhibited hydroformylation activity. Zeolite A has pore openings of ~ 4 Å, which are too small for any of the phosphine ligands to pass through. Thus, the rhodium carbonyl species most probably become detached from the cavity wall and migrate into solution, resulting in the formation of homogeneous catalysts. Post-reaction solutions obtained from the other zeolite systems were all tested for further hydroformylation activity, and except for zeolite A no activity was observed.

Hydroformylation of Styrene

The catalytic hydroformylation of styrene is of interest because the branched (chiral) reaction product (2-phenylpropionaldehyde or 2-phenylpropanol), rather than the linear isomer, is required, see Scheme IV. Table III shows results for zeolites X and Y.

In this catalyst system, the use of zeolite X as a support material is particularly beneficial, as it gives both superior activity (100 per cent conversion) and selectivity (*n:iso* = 1:5.7) over zeolite Y (75 per cent conversion, *n:iso* = 1:5.3). With the zeolite X catalyst system, the trade-off

Table III

Hydroformylation of Styrene Using (CO)₂Rh-Zeolite as Catalyst Precursor[a]					
Zeolite	Solvent	PR_3	Products	Conversion, per cent	Ratio *n:iso*
X	Toluene	PEt_3	3-phenylpropionaldehyde + 2-phenylpropionaldehyde	80	1:5
		PPr^n_3		75	1:4.6
		PPr^i_3		66	1:3
		None		15	1:7
	EtOH	PEt_3	3-phenylpropanol + 2-phenylpropanol	100	1:5.7
Y				75	1:5.3

[a] Styrene (1 cm³), solvent (4 cm³), 120°C, 17 h, [Rh] = 3.5 x 10⁻³ mol dm⁻³, [PR₃] = 3.5 x 10⁻² mol dm⁻³, 50 bar CO/H₂

Table IV
Hydroformylation of Prop-2-en-1-ol and Derivatives Using (CO)₂Rh-Zeolite as Catalyst Precursor[a]

Substrate	Zeolite	Conversion, per cent	Products	Ratio n:iso
1-Hexene	X	100	HEP (70%); MHL (30 %)	2.3:1
But-3-en-1-ol	homogeneous[b]	100	PDL (67 %); MBDL (33 %)	2:1
But-3-en-1-ol	X	95	ETHP (55 %); DEPL (13 %); METHF (19 %); DEMB (8 %)	2.6:1
Prop-2-en-1-ol	homogeneous[b]	100	BDL (68 %); MPD (32 %)	2.1:1
Prop-2-en-1-ol	X	100	ETHF (62 %); DEBL (10 %); DEMP (28 %)	2.5:1
Prop-2-en-1-ol	Y	54	ETHF (32 %); DEBL (3 %); DEMP (4 %); DEPA (15 %)	8.7:1
Prop-2-en-1-ol	ZSM-5	100	ETHF (60 %); DEBL (10 %); DEMP (20 %); DEPA (10 %)	3.5:1
Prop-2-en-1-ol	homogeneous[b] + added zeolite X	100	BDL (70 %); MPD (30 %)	2.3:1
Prop-2-en-1-ol[c]	X	81	PRA (23 %); PRL (58 %)	–
γ-Butyrolactone	X	no reaction		

between maximising either selectivity or activity is no longer needed. Again, the solvent is crucial in determining product selectivity: in toluene, aldehydes are formed, whereas in EtOH, only alcohols are formed. Table III also shows that a decrease in steric bulk of the phosphine ligands results in slight improvements in selectivity to a higher proportion of branched products. This may, however, also be due to the less basic phosphines (PEt₃ < PPr"₃ < PPrⁱ₃), resulting in increased preference for the more electron-donating branched-alkyl intermediates.

Hydroformylation of Prop-2-en-1-ol (Allyl Alcohol) and Derivatives

Selected results are shown in Table IV. In the homogeneous catalyst system, hydroformylation of prop-2-en-1-ol gives predominantly butan-1,4-diol (BDL) as product and 2-methylpropan-1,3-diol (MPD), corresponding to linear and branched products, respectively (6). However, with the zeolite-encapsulated catalysts, the results are markedly different, with the hydroformylation products being 2-ethoxytetrahydrofuran (ETHF), 4,4-diethoxybutan-1-

ol (DEBL) and 1,1-diethoxy-2-methylpropan-3-ol (DEMP). Traces of 1,1-diethoxypropane (DEPA) are also observed. These arise from the reaction of EtOH with propionaldehyde (the keto tautomer of prop-2-en-1-ol) to form the diacetal. These products derive from initial formation of the aldehyde products, as represented in Scheme V. In EtOH, these species rapidly undergo reaction with one molecule of EtOH to form the hemiacetal which can either cyclise as shown in pathway A to form ETHF, or react with a second molecule of EtOH (pathway B) to form the diacetal, DEBL. Thus, ETHF and DEBL are the straight chain products. The fate of the branched chain aldehyde is somewhat different. As with the straight chain species, it undergoes reaction with EtOH to form the hemiacetal. At this stage it does not cyclise, because the resulting four-membered ring would be considerably strained. Instead, it reacts with a second molecule of EtOH to form the diacetal, DEMP. The possibility that cyclisation occurs prior to acetal formation is ruled out by the observation that when γ-butyrolactone is used as a substrate, no reaction occurs. Reaction with

toluene in place of EtOH yielded only propanal (PRA; the aldehyde tautomer of prop-2-en-1-ol) and propanol (PRL; the hydrogenation product).

Zeolites Y and ZSM-5 give higher selectivities than zeolite X. This is due to the higher concentration of sodium ions in zeolite X, rendering the carbonyl carbon atom of the alkyl intermediate, see Figure 4, more δ+ than in Y or ZSM-5. This results in migration of the more electron-donating branched (compared with linear) alkyl group being more favoured in X than in Y or ZSM-5. It has been noted by others that countercations (Na⁺) in catalysts of this type can influence product selectivity (9).
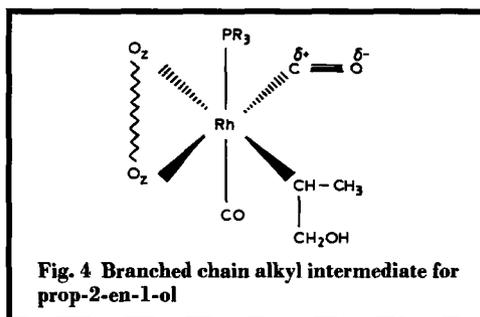
But-3-en-1-ol reacts similarly, the straight chain hydroformylation products being 2-ethoxytetrahydropyran (ETHP) (major) and 1,1-diethoxypentanol, (DEPL) (minor). The major branched chain product is now the cyclic product, 3-methyl-2-ethoxytetrahydrofuran (METHF) as the branched chain hemiacetal will readily cyclise to form a five-membered ring. The minor branched product is 1,1-diethoxy-3-methylbutan-4-ol (DEMB). The homogeneous catalyst system gives pentan-1,5-diol (PDL) and 3-methylbutan-1,4-diol (MBDL).
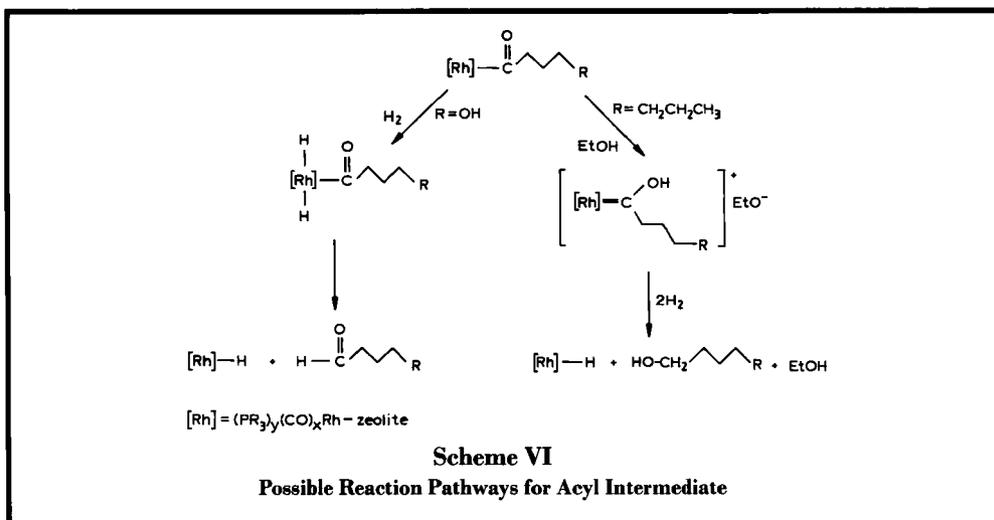
The reason for the differences in chemoselectivity, compared with the homogeneous system, is the chemical nature of the zeolite. The formation of acetals from aldehydes is an acid catalysed reaction; in this case it is catalysed by the zeolite. Thus, the zeolite participates in the catalytic reaction and dramatically alters the nature of the products. It appears that all of the reactions occur within the zeolite cavities/tunnels, as different chemo- and regioselectivities are observed if the catalyst is prepared in solution and the reaction is then carried out in the presence of added zeolite.

Scheme V

Formation of Acetals from Linear Aldehyde Products (from prop-2-en-1-ol)
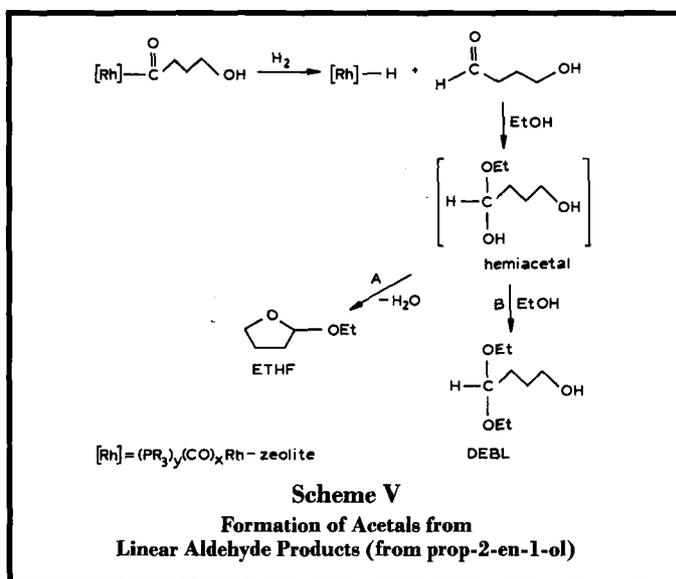
The acetal products are formed from the reaction of EtOH with the aldehydes, rather than by cyclodehydration of the alcohols (cyclodehydration of non-aromatic diols over solid acid catalysts is known (10)) as butan-1,4-diol remains unreacted with these catalyst systems.

As noted in a previous section, when using 1-hexene as a substrate, the products obtained in EtOH are the corresponding C₇ alcohols, namely 1-heptanol (HEP) and 2-methylhexan-1-ol (MHL). This is due to the effect of the R substituent (CH₂CH₂CH₃, as against OH) in the acyl intermediate, as shown in Scheme VI. If R = CH₂CH₂CH₃ (as in 1-hexene) then the carbonyl oxygen atom will be sufficiently δ– to effect the formation of hydroxycarbene species

Fig. 4 Branched chain alkyl intermediate for prop-2-en-1-ol

[Rh]—C(=O)∿∿R

H₂ R=OH

R= CH₂CH₂CH₃

EtOH

H | [Rh]—C(=O)∿∿R | H

[Rh]—C(OH)∿∿R EtO⁻

2H₂

[Rh]—H · H—C(=O)∿∿R

[Rh]—H · HO-CH₂∿∿R · EtOH

[Rh] = (PR₃)ᵧ(CO)ₓRh – zeolite

Scheme VI

Possible Reaction Pathways for Acyl Intermediate

by abstraction of a proton from a molecule of EtOH, resulting in the eventual formation of alcohol products. If R = OH, this group is electron-withdrawing. Combined with the effect of the intrazeolite Na^+ cations, this results in the carbonyl oxygen atom not being sufficiently δ– to abstract a proton from a molecule of EtOH. Thus, oxidative addition of hydrogen occurs, followed by reductive elimination of aldehyde species, which can then undergo acetal formation. A similar argument will apply for the use of styrene (versus allyl alcohol) as a substrate.

In all of the above reactions, the catalysts can be recovered at the end of the reaction and reused several times to give identical results. The infrared spectra of the recovered "ship-in-a-bottle" catalysts show the presence of bands attributable to intrazeolite complexes of the type $[(CO)_x(PR_3)_yRh-O_z]$, which are also formed during the reaction of the dicarbonyl encapsulated species PR_3 in toluene (11, 12). These carbonyl phosphine species were also tested for catalytic activity and gave identical results in terms of activity and selectivity.

Concluding Remarks

It has now been established that the zeolite support in "ship-in-a-bottle" catalysts should not be regarded merely as an inert support or mechanical backbone. Rather, it is a multidentate ligand (that can be referred to as a *zeolate* (13)) which will significantly affect the active site around the transition metal.

The immobilisation of an expensive catalyst applied in a homogeneous reaction is desirable. The separation of products from the catalyst is easy to achieve and thus decomposition induced by distillation or other methods of recovery is avoided. However, liquid-phase "ship-in-a-bottle" catalytic systems have two major problems associated with them: (a) the leaching of the transition metal out of the zeolite cavity into solution, and subsequently, (b) is this a genuine "ship-in-a-bottle" catalyst or a homogeneous catalyst formed by the metal species in solution? While *some* homogeneous catalysis cannot be ruled out at this stage, as small amounts of rhodium (about 5 ppm) were observed in the post-reaction solutions for zeolite A, but this, as noted previously, was the exception. There are several strong indications that "ship-in-a-bottle" catalysis is dominant in these catalyst systems:

[i]   improved *n:iso* ratios relative to the homogeneous systems are observed

[ii]   different *n:iso* ratios and different conversions are observed with different zeolites

[iii]   different chemo- and regioselectivities are obtained if the catalyst is prepared in solution and the reaction carried out in the presence of

added zeolite as the prepared catalysts are too large to enter the pores of the zeolite supercages.

In situ EXAFS studies are currently underway to probe the exact mechanism by which these hybrid catalyst systems operate (14).

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Palladium Catalysts in Modern Organic Synthesis

Database of Palladium Chemistry: Reactions, Catalytic Cycles and Chemical Parameters CD-ROM version 1.0

BY J.-L. MALLERON AND A. JUIN, Academic Press, London, 1996, ISBN 012-466760-0, £545.00

Palladium mediated reactions are particularly valuable for the direct introduction of carbonyl groups, for forming carbon-carbon bonds via coupling processes typified by Heck reactions, and for selective oxidations such as those based on conventional Wacker reactions. Recent exciting results with asymmetric palladium-catalysed reactions will keep palladium at the forefront of new methodologies in synthetic organic chemistry. Therefore, many texts are available concerned with applications of palladium species in organic synthesis, such as those in (1, 2).

The present CDROM is not a text but a database of some 3500 published organic transformations in which 'palladium' is the catalyst. All the usual mechanistic types are represented and the records take the form of reference citations with equations showing structures of reactants and products, and other information. Author names, catalysts/ligands, structures, solvents, reactants and products can be searched, and this is a fairly rapid process. Substructures can be searched by using ISIS/Draw to draw the reaction, transferring it to the box "reaction", then searching.

The database needs a PC with MS Windows 3.1 or later. The publishers suggest a Pentium processor with 16 MB of RAM and 20 MB of hard disk space if installation is to a hard drive; instructions are contained on the CDROM. Gaining familiarity with the database takes time, but the present reviewer did not find searching intuitive. The full database was not assessed as the review copy was a demonstration version.

However, there is certainly a place for such databases, but this one is not cheap. Potential users are probably already using on-line databases. So the price of a CDROM (and updates) has to be compared with on-line search costs. At present, this reviewer would tend to favour the latter, but as larger amounts of information become available at lower prices, the balance could move towards the use of CDROMs.

M. V. TWIGG

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