

# Improved regioselectivity in the hydroformylation reaction catalysed by zeolite-encapsulated rhodium(I) species

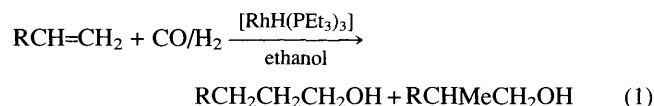
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Although zeolite-encapsulated  $[\text{Rh}(\text{CO})_x(\text{PR}_3)_y]$  ( $\text{PR}_3 = \text{PEt}_3, \text{PEt}_2\text{Ph}, \text{PPr}^n_3$  or  $\text{PPh}_3$ ) give similar chemoselectivities in the hydrocarbonylation of hex-1-ene relative to their homogeneous analogues, the linear:branched ratio can be increased by as much as 10 times.

Industrial processes utilising soluble transition-metal catalysts are all beset with the problem of recovering the catalyst from the reaction products. Considerable effort is thus currently being made to explore solutions to this problem. One area receiving attention is the encapsulation of known homogeneous catalyst systems within the pores of zeolites and other molecular sieves, the so-called 'ship-in-a-bottle' catalysts.

The hydroformylation of alkenes to produce aldehydes and/or alcohols is one of the most versatile methods for the functionalisation of C=C bonds. The most efficient hydroformylation catalysts contain rhodium and these tend to give aldehydes as the major products. Short-chain products are preferred as aldehydes for condensation reactions, but longer-chain products are usually preferred as alcohols. It has recently been shown that, under hydroformylation conditions using  $[\text{RhH}(\text{PEt}_3)_3]$  as a catalyst precursor, alkenes can, depending on the reaction conditions, give selectivity to alcohols rather than aldehydes if the reaction is carried out in alcoholic solvents [eqn. (1)].<sup>1-3</sup>



The above system gave a linear: branched ratio of, typically, 2.4:1.

We present here our investigations into the use of zeolite-encapsulated rhodium(I) species as liquid-phase hydroformylation catalysts in an attempt to improve (a) the catalyst recovery and (b) the linear: branched ratio of the products from these types of catalyst.

Although reports have appeared on the use of zeolite-encapsulated rhodium species as liquid-phase hydroformylation catalysts, these studies investigated different catalyst precursors and different reaction conditions and resulted only in the formation of aldehydes.<sup>4,5</sup> However, some improvement in selectivity over the analogous homogeneous systems was observed. In addition, the effect of the support material itself has not been investigated in any detail; zeolite Y has been the only zeolite thus far to receive serious attention.

For our studies, the catalysts were prepared as follows. (i) Ion-exchange of sodium (in the sodium forms) of zeolite X (Si:Al = 1) and Y (Si:Al = 2.5) for rhodium (as  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ) (90 °C, 20 h, pH 6). It has been suggested that this type of exchange process locates the rhodium mostly within the zeolite supercages.<sup>6</sup> The resultant rhodium-zeolite species contained ca. 2.7 mass% (X) and 3.0 mass% (Y) of rhodium, which correspond to roughly one rhodium atom per supercage. (ii) The rhodium-exchanged species were then carbonylated (120 °C, 10 h, 10 atm CO). This procedure results in the formation of zeolite-encapsulated rhodium(I) dicarbonyl species,<sup>7</sup> as shown

in Fig. 1 (where  $\text{O}_z$  is a framework oxygen atom of the zeolite cavity) which has  $\nu_{\text{CO}}$  at 2085 and 2019  $\text{cm}^{-1}$  (zeolite X) and 2093 and 2029  $\text{cm}^{-1}$  (zeolite Y).

Thus, two framework oxygen atoms (one bearing a negative charge) are coordinated to the rhodium(I) ion, thereby completing the expected square-planar coordination of a  $d^8$  cation. The zeolite framework is therefore acting not only as a mechanical backbone, but also as a bidentate ligand and a matrix leading to effective isolation of the rhodium sites. With zeolite Y, as small amount of another type of rhodium(I) species, viz.  $\text{Rh}^{\text{I}}(\text{CO})_2^+\text{O}_z^-(\text{H}_2\text{O})$  ( $\nu_{\text{CO}} = 2056 \text{ cm}^{-1}$ ) (a lattice oxygen oxygen atom has been replaced by a water molecule) and a small amount of the hexanuclear cluster,  $\text{Rh}_6(\text{CO})_{16}$  ( $\nu_{\text{CO}} = 1785 \text{ cm}^{-1}$ ), were also formed within the zeolite supercage. The rhodium-exchanged zeolite X species does not form clusters during the carbonylation procedure, regardless of pretreatment conditions, whereas the zeolite Y species must be dehydrated prior to carbonylation otherwise the only species present is  $\text{Rh}_6(\text{CO})_{16}$ . (Similar results were obtained by Rode *et al.*<sup>7</sup>) The reason for this phenomenon is presumably the acidity of the zeolites. Zeolite X, with an Si:Al ratio of 1, is of relatively low acidity; the higher acidity of zeolite Y (Si:Al = 2.5) results in the oxygen atoms of the cavities being sufficiently nucleophilic to effect a small degree of cluster formation (viz. reduction of  $\text{Rh}^{\text{I}}$  to  $\text{Rh}^0$ ).

These species, viz.  $(\text{CO})_2\text{Rh}-\text{O}_z$ , were then investigated at hex-1-ene hydroformylation catalysts in the presence of various phosphines. The results are shown in Table 1. It is apparent from these results 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 (i) the regioselectivity, viz. the *n*:*iso* ratio, is higher than that obtained with the homogeneous systems,<sup>2-4</sup> (ii) 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 *cf.* X) and (iii) 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  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  and phosphines.<sup>1-3</sup> Thus, primary phosphines give  $\text{C}_7$  alcohols if the reactions are carried out in ethanol but mainly aldehydes if the solvent is toluene;  $\text{PPh}_3$  promotes the formation of aldehydes and acetals even in alcoholic solvents. Presumably, in these cases, the alcohols derive from hydrogenation of the aldehydes with the linear aldehydes being hydrogenated preferentially, resulting in higher *n*:*iso* ratios for alcohols *cf.* aldehydes.

The overall conversions are generally lower than in the homogeneous system, although, in the case of zeolite Y, some unusual pressure dependences are observed. Thus, the yield decreases with increasing pressure (and increasing regioselectivity).

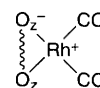


Fig. 1 Zeolite-encapsulated rhodium(I) dicarbonyl species

**Table 1** Hydroformylation of hex-1-ene using (CO)<sub>2</sub>Rh–zeolite as catalyst precursor<sup>a</sup>

Solvent	Zeolite	<i>p</i> /atm	PR <sub>3</sub>	Yield of C <sub>7</sub> alcohols (%)	<i>n</i> : <i>iso</i> ratio	Yield of C <sub>7</sub> aldehydes (%)	<i>n</i> : <i>iso</i> ratio
Toluene	X	50	PEt <sub>3</sub>	21	3.5	79	3.3
EtOH		50	PPh <sub>3</sub>	52	100% linear	38 <sup>b</sup>	2.9
		10	PEt <sub>3</sub>	100	2.2	—	—
		20	—	100	2.4	—	—
		50	—	80	2.5	—	—
		80	—	48	3.4	—	—
		50	PPr <sup>n</sup> <sub>3</sub>	32	3.5	—	—
		20	PEt <sub>2</sub> Ph <sup>c</sup>	60	10.1	—	—
50		—	40	21	—	—	
80		—	25	24	—	—	
Toluene	Y	50	PEt <sub>3</sub>	15	3.9	60	3.8
EtOH		50	PPh <sub>3</sub>	36	100% linear	35 <sup>d</sup>	5
		10	PEt <sub>3</sub>	15	4	—	—
		20	—	20	4.2	—	—
		50	—	70	5.1	—	—
		80	—	40	14	—	—
		50	PPr <sup>n</sup> <sub>3</sub>	80	5.3	—	—
		50	PEt <sub>2</sub> Ph <sup>c</sup>	30	24	—	—
80		—	20	26	—	—	
—		Y <sup>e</sup>	50	PEt <sub>3</sub>	—	—	—

<sup>a</sup> Hexene (1 cm<sup>3</sup>), solvent (4 cm<sup>3</sup>), 120 °C, 17 h, [Rh] = 3.5 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [PR<sub>3</sub>] = 3.5 × 10<sup>-2</sup> mol dm<sup>-3</sup>. <sup>b</sup> Diethyl acetals of C<sub>7</sub> aldehydes are also formed (10%). <sup>c</sup> Diethyl acetals of C<sub>7</sub> aldehydes are also formed (30%) with this phosphine. <sup>d</sup> Diethyl acetals of C<sub>7</sub> aldehydes are also formed (30%). <sup>e</sup> Catalyst precursor [Rh(H)(PEt<sub>3</sub>)<sub>3</sub>], zeolite Y added to reaction mixture. Products are exclusively diethyl acetals (100%) of C<sub>7</sub> aldehydes (*n*:*iso* = 3.1).

tivity) when using PEt<sub>3</sub> in zeolite X, but tends to increase initially and then decrease with pressure in zeolite Y.

The main difference between the homogeneous and the ship-in-a-bottle systems is that the linear:branched ratio can be somewhat higher in the latter. In the homogeneous system, the *n*:*iso* ratio was generally *ca.* 2–3 and only increased when conversions were low. Many of the reactions listed in Table 1 exhibit higher *n*:*iso* ratios and, although in some cases this may correlate with low conversions, in others it appears that this is a genuine effect brought about by the zeolite (*e.g.* PEt<sub>3</sub> at 50 atm in zeolite Y).

The most exciting results are obtained upon using larger phosphines in the zeolite systems, *e.g.* the *n*:*iso* ratio using PPr<sup>n</sup><sub>3</sub> is higher than when using PEt<sub>3</sub>. Similarly, using PEt<sub>2</sub>Ph, very high *n*:*iso* ratios {comparable to those using the commercial system based on [RhH(CO)(PPh<sub>3</sub>)<sub>3</sub>]} are obtained in both zeolite X and Y. The most noticeable effect is that the more acidic zeolite Y gives increased *n*:*iso* ratios when compared with the homogeneous system or zeolite X. However, the drawbacks to this system are (i) diethyl acetals of C<sub>7</sub> aldehydes are also formed (*ca.* 30%), and (ii) although the larger phosphine results in a higher *n*:*iso* ratio by virtue of increased steric bulk, it also results in less stable complexes which increases the amount of rhodium leaching (determined by atomic absorption analysis; typically, values of *ca.* 10–15 ppm Rh with PEt<sub>2</sub>Ph in the solution at the end of the reaction are observed, as compared to *ca.* 5 ppm for PEt<sub>3</sub>). A value of 10–15 ppm Rh post-reaction is rather less than ideal and raises the possibility that some of the catalysis observed may be homogeneous in nature. While *some* homogeneous catalysis cannot at this stage be ruled out, 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 obtained, (ii) different *n*:*iso* ratios and different conversions are observed with different zeolites, and (iii) different chemo- and regio-selectivities are observed if the catalyst is prepared in solution and the reaction is then

carried out in the presence of added zeolite (the prepared catalyst is too large to enter the pores of the zeolite supercages). The catalysts can be used *ca.* 5 times before the activity starts to diminish. Bearing in mind the higher selectivity possible by optimisation of the phosphine ligand, the problem of rhodium leaching is presently under investigation.

The IR spectra of the recovered ship-in-a-bottle catalysts also show the presence of bands [ $\nu_{\text{CO}}$  1960 cm<sup>-1</sup> (X), 1990 cm<sup>-1</sup> (Y)] attributable to intrazeolite complexes of the type (CO)<sub>x</sub>-(PR<sub>3</sub>)<sub>y</sub>Rh-O<sub>z</sub> (PR<sub>3</sub> = PEt<sub>3</sub>, PPr<sup>n</sup><sub>3</sub>, PEt<sub>2</sub>Ph), which are also formed on reaction of the dicarbonyl encapsulated species with PR<sub>3</sub> in toluene. These carbonyl phosphine species were also tested for catalytic activity and gave identical results in terms of selectivity and activity, which lends support to the proposal that the catalytically active species is of the type (CO)<sub>x</sub>(PR<sub>3</sub>)<sub>y</sub>Rh<sup>+</sup>-O<sub>z</sub><sup>-</sup>.

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