Hydrocarbonylation of prop-2-en-1-ol catalysed by zeolite-encapsulated rhodium species: chemoselectivity effects imposed by the zeolite support

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Zeolite-encapsulated catalysts, $[Rh(CO)_x(PR_3)_y]$-zeolite, exhibit markedly different chemoselectivities to their homogeneous counterparts; furans and pyrans are formed from the hydrocarbonylation of prop-2-en-1-ol or but-3-en-1-ol instead of the expected diols. The nature of the zeolite support was found to influence the selectivity of the reaction.

Keywords: zeolites, encapsulated, rhodium, hydrocarbonylation

It has been shown that, under hydroformylation conditions using $[Rh_2(O_2CMe)_4]/PEt_3$ as a catalyst precursor, alkenes can give selectivity to alcohols rather than aldehydes if the reaction is carried out in alcoholic solvents such as ethanol [1–4]:

$$RCH{=}CH_2 + CO/H_2 \xrightarrow[\text{ethanol}]{[Rh_2(O_2CMe)_4]/PEt_3} RCH_2CH_2CH_2OH + RCH(CH_3)CH_2OH$$

$$(R = CH_3CH_2CH_2CH_2, CH_2OH) \qquad (1)$$

The reason for this unusual selectivity is the formation of a hydroxycarbene species which frustrates reductive elimination of aldehyde species [1]. The above system gave an n : iso ratio of 2.4 : 1.

We have recently reported preliminary results on the use of zeolite-encapsulated rhodium(I) species as liquid-phase hexene hydroformylation catalysts, which exhibited both improved selectivities and improved catalyst recovery [5]. Studies on zeolite-encapsulated rhodium species as hydroformylation catalysts are known [6–8]. However, the precise effects of the nature of the zeolite support, and of the substrate itself, were not investigated. Our previous study focused on zeolites X and Y; it was found that the nature of the zeolite (the Si : Al ratio) exerted a strong effect on the selectivity of the reaction. The n : iso ratio was considerably higher with zeolite Y as compared to zeolite X. We now extend this study to include the zeolite ZSM-5 and functionalised alkenes, viz. prop-2-en-1-ol (allyl alcohol) and but-3-en-1-ol, as substrates.

The catalysts were prepared as follows: (i) ion-exchange of sodium (in the sodium forms) of zeolite X (Si : Al = 1), Y (Si : Al = 2.5) and ZSM-5 (Si : Al = 100) for rhodium (as $RhCl_3 \cdot 3H_2O$) (90°C, 20 h, pH 6); (ii) the rhodium-exchanged species were carbonylated (120°C, 10 h, 10 atm CO) to give zeolite-encapsulated rhodium(I) dicarbonyl species, represented in fig. 1 (where O_z is a framework oxygen atom of the zeolite cavity) [6]. These species have ν_{CO} at 2085 and 2019 cm^{-1} (zeolite X), 2093 and 2029 cm^{-1} (zeolite Y) and 2070 and 2020 cm^{-1} (ZSM-5). With zeolites Y and ZSM-5, small amounts of the hexanuclear cluster $[Rh_6(CO)_{16}]$ were also formed. The reason for this is the electronic environment within the zeolite cavities. The higher concentration of Na^+ ions in zeolite X (than in Y or ZSM-5) renders nucleophile-induced cluster formation less likely.

These zeolite-encapsulated rhodium species were then investigated as hydroformylation catalysts in the presence of added phosphine ligands. The results are shown in table 1. In the homogeneous catalyst system, hydroformylation of prop-2-en-1-ol gives predominantly butane-1,4-diol (BDL) and 2-methylpropan-1-ol (MPD) as products. However, with the zeolite-encapsulated catalysts, the results are markedly different. The hydroformylation products are 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; this product arises reaction of EtOH with propionaldehyde (the

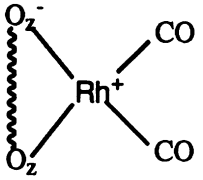

Fig. 1. Zeolite-encapsulated rhodium(I) dicarbonyl species.

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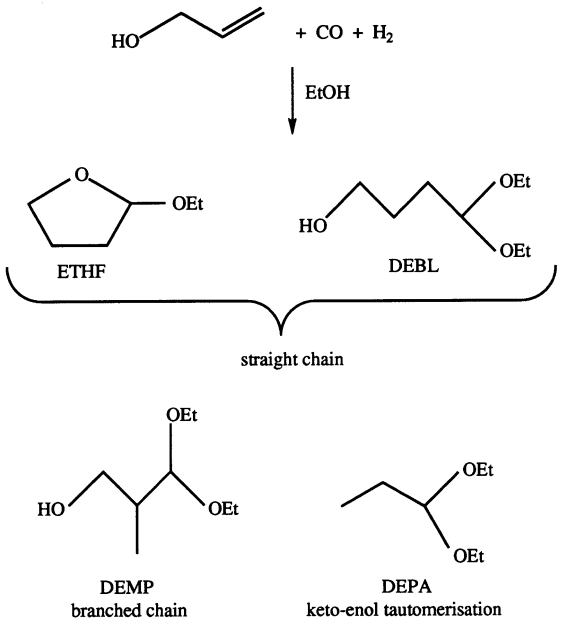
Table 1
Results of hydroformylation reactions [a]

Substrate	Zeolite	Conversion (%)	Products	*n* : iso ratio
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		

[a] Catalyst precursor was $[(CO)_2Rh\text{-zeolite}]/PEt_3$ unless stated otherwise; substrate (1 cm^3); solvent (ethanol, 4 cm^3), 120°C, 17 h, $[Rh] = 3.5 \times 10^{-3}$ mol dm^{-3}, $[PEt_3] = 3.5 \times 10^{-3}$ mol dm^{-3}, 50 bar CO/H_2.
[b] Catalyst is $[Rh_2(O_2CMe)_4]/PEt_3$.
[c] Toluene used as solvent.

keto tautomer of prop-2-en-1-ol) to form the diacetal. We propose that these products derive from initial formation of the aldehyde products, as represented in scheme 1. In ethanol, 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; the resultant 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, it remains unreacted. Reaction in toluene instead of ethanol yielded only propanal (PRA; the aldehyde tautomer of prop-2-en-1-ol) and propanol (PRL; hydrogenation product).

Zeolites Y and ZSM-5 give higher selectivities than does zeolite X. This is due to the higher concentration of sodium ions in zeolite X, rendering the carbonyl carbon atom of the alkyl intermediate (fig. 2) more δ^+ than in Y or ZSM-5. This results in migration of the more electron-donating branched (cf. 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]. Zeolite Y produces a higher *n* : iso ratio than ZSM-5; however, we believe this is due to the lower conversion observed. This correlation, viz. high selectivity with low conversions, has been noted previously [3,5]. The reason for the low conversion observed with zeolite Y is currently under investigation.



Scheme 1. Products from hydroformylation of prop-2-en-1-ol using zeolite-encapsulated rhodium catalysts.

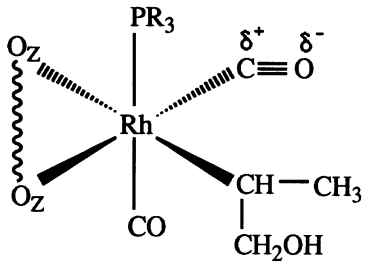
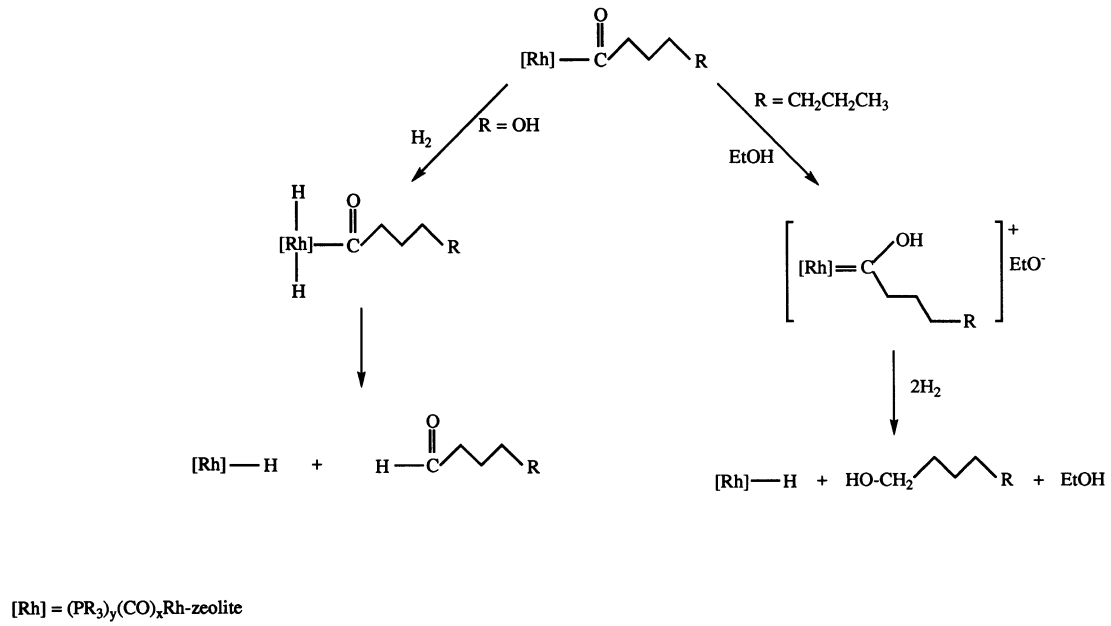


Fig. 2. Branched chain alkyl intermediate for prop-2-en-1-ol.



[Rh] = $(PR_3)_y(CO)_xRh$-zeolite

Scheme 2. Possible reaction pathways for acyl intermediate.

But-3-en-1-ol reacts similarly. The straight chain hydroformylation products are 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 system gives pentan-1,5-diol (PDL) and 3-methyl-butan-1,4-diol (MBDL).

The reason for the differences in chemoselectivity cf. the homogeneous system is the chemical nature of the zeolite. The formation of acetals from aldehydes and alcohols is an acid-catalysed reaction which, in this case, 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 (table 1). We propose that the acetal products are formed from the reaction of ethanol with the aldehydes rather than by cyclodehydration of the alcohols (cyclodehydration of non-aromatic diols over solid acid catalysts is known [10]), as 1,4-butanediol remains unreacted with these catalyst systems.

With 1-hexene the products obtained are the corresponding C_7 alcohols, viz. 1-heptanol (HEP) and 2-methylhexan-1-ol (MHL). This is due to the effect of the R substituent ($CH_2CH_2CH_3$ versus OH) in the acyl intermediate, as shown in scheme 2. If $R = CH_2CH_2CH_3$ (as in 1-hexene) then the carbonyl oxygen atom is sufficiently δ^- to effect the formation of hydroxycarbene species 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 an EtOH molecule. Thus, oxidative addition of H_2 occurs, followed by reductive elimination of aldehyde species, which then undergo acetal formation.

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