Intrazeolite catalysts with sulfur donor ligands – synthesis and catalytic activity

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Several intrazeolite rhodium complexes with sulfur donor ligands have been synthesised; these species are found to act as active and selective hydroformylation catalysts which can readily be recovered and re-used; they also result in the preferential formation of the branched hydroformylation product.

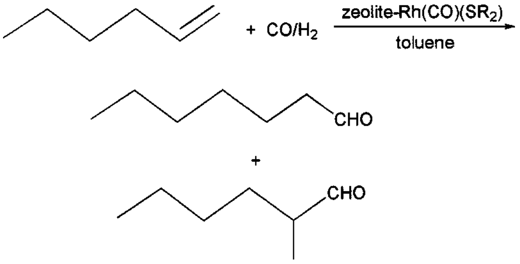
Keywords: zeolite, rhodium, encapsulated, chiral, thioether

Many organometallic and coordination compounds have been used successfully in homogeneous catalysis. Often these catalyst systems are highly selective and allow mild reaction conditions to be used. However, difficult separation of the catalyst from the reaction products or deactivation due to irreversible structural changes can compromise the benefits of homogeneous catalyst systems. Interest is thus now focusing on immobilising homogeneous catalysts in order to combine their high activity and selectivity with the processing advantages of a heterogeneous catalyst. In this regard, microporous solids such as zeolites are attracting researchers interested in developing hybrid catalyst systems. A salient feature of the crystalline structures of zeolites is the occurrence of strictly regular cavities and pores of molecular dimensions. Thus, in contrast to the commonly used classical amorphous supports (such as oxides), zeolites offer a unique potential to alter selectivities and to modify catalytic transition states.

Organometallic species can be quantitatively located within the supercages of large-pore zeolites either by direct means [1] or by intrazeolite synthesis [2]. We have recently reported our results on the investigation of rhodium(I) carbonylphosphine complexes as hydroformylation catalysts [2,3]. These catalysts are highly efficient, often giving selectivities far superior to their homogeneous counterparts. However, a drawback with these systems is that the phosphine ligands were often susceptible to oxidation. We have thus decided to investigate analogous thioether ligands (SR_2), which are known to form active and selective homogeneous catalysts [4], but which are more robust than the phosphine systems. To the best of our knowledge, this is the first report of thioether ligands, or indeed any sulfur-containing species, being used as ligands in intrazeolite catalysts. Four ligands were investigated: SMe_2 (**I**), SPh_2 (**II**), thianthrene (**III**) and the chiral ligand $DIOSPh_2$ (**IV**). The structures of **III** and **IV** are shown in figure 1.

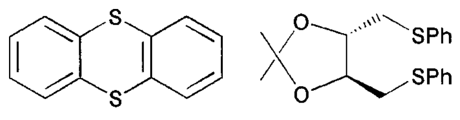
For ligands **I**, **II** and **III**, the intrazeolite catalysts were synthesised by a method previously described by us, as represented in scheme 1 [2,3]. Three different zeolites were used, viz. zeolites X (Si : Al = 1), Y (Si : Al = 2.5) and β (Si : Al = 15). For the DIOS catalysts, two different synthetic routes were followed, viz. the method outlined in scheme 1 and *intrazeolite ligand synthesis*, as outlined in scheme 2. In this latter procedure, the $DIOSPh_2$ ligand was synthesised inside the zeolite cavities (starting from diethyl L-tartrate) *before* the rhodium was introduced. This procedure thus represents *intrazeolite ligand synthesis*.

These catalyst systems were then used for the hydroformylation of 1-hexene to the corresponding C_7 aldehydes (equation (1)); results are shown in table 1. In most cases, small amounts of isomerisation products (ca. 10%) (from the hydroformylation of 2-hexene, formed by the isomerisation of 1-hexene) were observed. Trace amounts of n-hexane (<5%), resulting from the hydrogenation of hexene, were also observed.



(1)

Once the reaction was complete, the zeolite-encapsulated catalysts can easily be recovered by a simple filtration. They



III IV

Figure 1. The structures of thianthrene (**III**) and $DIOSPh_2$ (**IV**).

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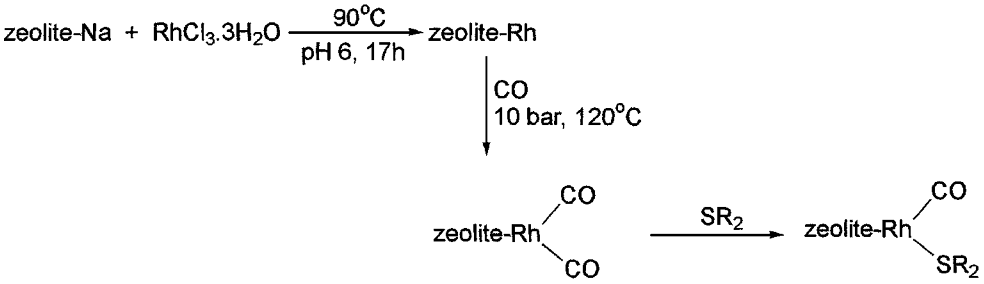
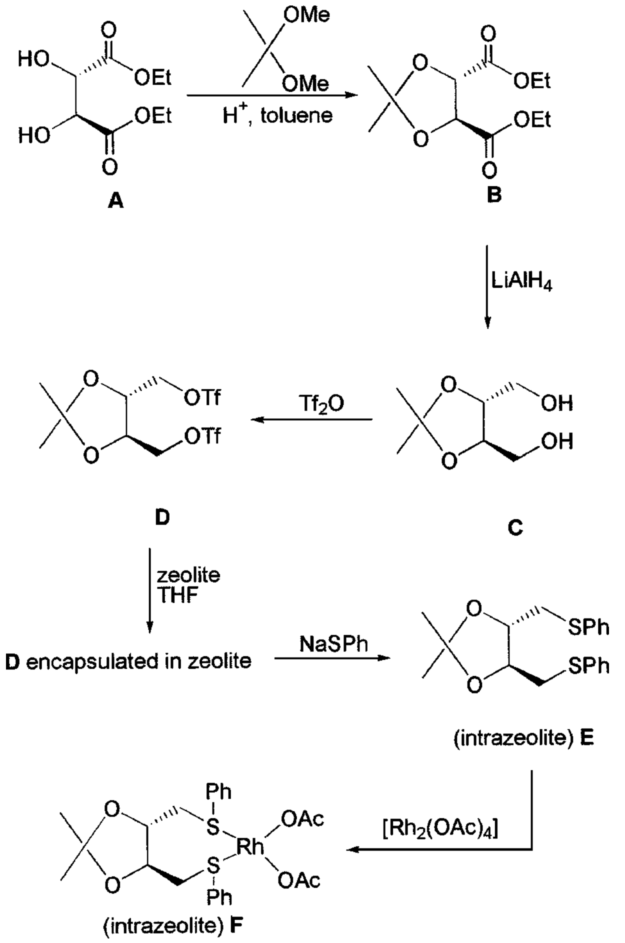


Scheme 1. Typical rhodium loadings are 1.5% for zeolite X, 2.8% for zeolite Y and 5% for zeolite β.



Scheme 2.

Table 1
Hydroformylation using intrazeolite rhodium thioether species.[a]

Substrate	Ligand SR_2	Zeolite	Conversion (%)	n : iso ratio
1-hexene	SMe_2	Homogeneous[b]	100	1 : 0.8
		X	100	1 : 1.2
		Y	100	1 : 1.1
		β	100	1 : 1.1
	SPh_2	Homogeneous[b]	100	1 : 0.9
		X	100	1 : 1.1
		Y	100	1 : 1.1
		β	100	1 : 1.2
	Thianthrene	Homogeneous[b]	100	1 : 0.9
		X	100	1 : 1.2
		Y	100	1 : 0.9
		β	100	1 : 0.8
	$DIOSPh_2$	Homogeneous[b]	100	1 : 0.8
		X	100	1 : 1.13
		Y	100	1 : 1.2
		β	100	1 : 1.0
	SPh_2	Homogeneous[c]	100	1 : 0.9
		X[c]	15	1 : 1.2

[a] Reaction conditions: substrate 1 cm^3, solvent (toluene) 4 cm^3, 120 °C, 40 bar CO/H_2, 17 h.
[b] Catalyst is $[Rh_2(OAc)_4]/SR_2$.
[b] Reaction time is 4 h.

were dried under nitrogen and then re-used to give identical results. The supernatant liquid was also recovered in each case and tested for catalytic activity; in no instance was any observed. While these two factors are not proof that intrazeolite catalysis is occurring, they certainly represent a very strong indication that this is the case.

The results from table 1 show that these systems comprise extremely active catalysts with 100% conversion being observed in each case. In order to obtain a more accurate comparison between the activities of the two catalyst systems, two reactions were run for 4 h. These showed the reaction with the homogeneous catalyst to be complete, whereas the zeolite-encapsulated catalyst only gave 15% conversion. This may, however, be due to an induction period being required for the zeolite-encapsulated systems.

The zeolite-encapsulated systems do not result in any significant improvement in selectivity over the analogous homogeneous catalysts. The results also do not vary significantly with variation in the zeolites used, which is in contrast to the intrazeolite rhodium phosphine systems [2,3]. They do, however, result in a much higher proportion of branched product being formed than with the phosphine systems, e.g., for hydroformylation with zeolite-Rh(CO)(PEt_3), branched product is ca. 16% of total products; for zeolite-Rh(CO)(SMe_2), branched product is ca. 52% of total products. This is a very encouraging result for the application of these systems to asymmetric catalysis with the use of chiral ligands such as $DIOSPh_2$. These catalysts now look more promising than their phosphine analogues for use in asymmetric catalysis using intrazeolite catalysts. We are also investigating the application of these systems to the asymmetric hydroformylation of vinyl aromatics and, in this instance, quite marked differences in selectivity are observed compared to the homogeneous systems. These products are important intermediates in the synthesis of anti-inflammatories such as ibuprofen and naproxen. These results will be reported shortly [5].

In summary, although the selectivities exhibited by these intrazeolite thioether catalysts have not yet been optimised, they do represent an important new class of catalysts in that they are very active, robust (more so than the analogous phosphine systems) and they are more selective for the branched products than the phosphine-substituted catalysts. They represent the first example, as far as we are aware, of intrazeolite catalysts containing sulfur-donor ligands.

Acknowledgement

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