New "ship-in-a-bottle" type rhodium complexes as efficient catalysts for the hydrogenation of alkenes

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A new method for the encapsulation of homogeneous Rh complexes was developed and applied for the heterogenization of $[Rh(COD)L]^+$ complexes, where L = L-prolinamide or *N-tert*-butyl-L-prolinamide. The "ship-in-a-bottle" type catalysts were prepared by the intrazeolite synthesis method. The heterogenized catalysts were characterized by the usual spectroscopic methods and they have higher specific activity values in the hydrogenation of several different alkenes than the homogeneous counterparts. In the enantioselective hydrogenation of the (*Z*)-methyl-(2-acetamido-3-phenylacrylate) the ee values were much higher on the heterogenized catalyst than on the homogeneous one.

KEY WORDS: ship-in-a-bottle; enantioselective hydrogenation; heterogenized catalysts; rhodium complexes; prolinamide; zeolite Y.

1. Introduction

Hydrogenation of organic substances, especially asymmetric hydrogenations, is a widely studied area of organic catalysis. The growing interest in the fundamental study of these hydrogenations is explained by their extensive industrial applications. Many transition metal complexes, *e.g.*, [Rh(dien)(DIPAMP)] or $[Ru(BINAP)(OAc)_2]$, are known that are able to catalyze the asymmetric hydrogenation with high activity and selectivity under homogeneous conditions [1]. These catalysts are usually expensive materials and in practical applications it would be advisable to recover and to reuse them. That is why great attention has been devoted in the past decade to the field of heterogenization of these hydrogenation catalysts.

Several different supports, both organic and inorganic [2,3], have been used recently for the heterogenization of these complexes. However, the anchoring of these complexes usually leads to the decrease in activity of the catalysts [4,5]. In spite of the wide popularity of this area, there is still a need to develop a heterogenization method which produces stable and active heterogenized hydrogenation catalysts.

Microporous metal oxide supports such as zeolites could be one of the choices of support. Complexes trapped in the zeolite supercage are not necessarily bonded to the surface and are often referred to as "ship-in-a-bottle" complexes. This type of catalyst may provide site isolation, which can enhance the stability of these complexes.

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Previous works to immobilize the above-mentioned Rh complexes used a method which bound the complex to the surface of the host [6–8]. The heterogenized compounds gave higher enantiomeric excess (ee) values than the homogeneous systems; nevertheless they were less stereoselective than the other Rh complexes. Because the ship-in-a-bottle method often increases the stereoselectivity [9], in this paper we wish to report our efforts to develop a new way to heterogenize these organometallic complexes. The intrazeolite synthesis method [10,11] has not been used to build Rh complexes into a zeolite supercage so far. We describe the synthesis, characterization and catalytic activity of the two Rh complexes studied.

2. Experimental

2.1. Synthesis of complexes

L-Prolinamide was purchased from Aldrich and the *N-tert*-butyl-L-prolinamide ligand was synthesized according to the literature [6]. For the synthesis of the complexes a solution of 0.2 mmol rhodium complex precursor, $[Rh(COD)Cl]_2$, was deoxygenated in 20 ml of dry CH_2Cl_2 with argon. 0.4 mmol (77.87 mg) $AgBF_4$ was added to the mixture and stirred for 1 h under an argon atmosphere. 0.4 mmol L-prolinamide or *N-tert*-butyl-L-prolinamide was added to the solution and stirred for 3 h. The white precipitate was filtered from the yellow solution and the solvent was evaporated. The orange complex was identified by FTIR spectroscopy.

2.2. Encapsulation of the complexes

A solution of the 0.2 mmol of rhodium complex precursor, $[Rh(COD)Cl]_2$, was deoxygenated in 20 ml of dry CH_2Cl_2 with argon. 0.4 mmol (77.87 mg) $AgBF_4$ was added to the mixture and stirred for 1 h under argon. The white precipitate was filtered and 2.0 g of NaY zeolite was added to the mixture. The mixture was stirred for 3 h under argon. 0.4 mmol L-prolinamide or *N-tert*-butyl-L-prolinamide was added to the solution and stirred overnight. The catalyst was filtered and washed several times with CH_2Cl_2 to remove the surface complexes. The catalysts were dried in vacuum at 373 K overnight.

2.3. Catalyst characterization

The encapsulated catalysts were characterized by the usual spectroscopic methods, *e.g.*, FTIR and XRD spectroscopy, and the metal content was determined by ICP. The FTIR spectra of the zeolite, the neat complexes, the mixture of the zeolite and the neat complexes and the heterogenized samples were taken as well. The spectra were recorded in KBr pellets, using a Bio-Rad FTS 65 Å spectrophotometer, in the range 400–4000 cm^{-1}.

The XRD spectra were recorded on a Philips PW-1830 diffractometer. To determine the metal content the sample was dissolved in cc. HNO_3 and HF. The metal content was determined by a Jobin Yvon 24 type ICP-AES instrument. The flow rate of the argon was 12 dm^3/min and the sample dosing was carried out at a rate of 1.5 cm^3/min.

2.4. Hydrogenation experiments

Hex-1-ene, cyclohexene and 1-methylcyclohexene have been hydrogenated in a batch reactor of 60 ml capacity, at 323 K reaction temperature and 6 atm hydrogen pressure. 10 mg homogeneous or 250 mg heterogenized catalysts were added to 5 ml of 4-methylpentan-2-one, followed by 1 ml alkene. The reactor was pressurized by hydrogen gas and the stirring was started. Samples were taken from the reaction mixture every 2 or 3 h, and the products were analyzed by capillary gas chromatography (Hitachi 263-80) using a TCEP-60 column.

2.5. Enantioselective hydrogenation

10 mg homogeneous or 100 mg heterogenized catalysts and 10 mg (*Z*)-methyl-(2-acetamido-3-phenylacrylate) ((*Z*)-methyl-α-acetamidocinnamate) were added to 1 ml of butan-2-one in the batch reactor and the same procedure was followed as indicated above. The products were analyzed by gas chromatography using He as carrier gas and a 25 m Permabond-L-Chirasil-Val chiral capillary column at 150 °C.

3. Results and discussion

We have prepared the ship-in-a-bottle type catalysts from the $[Rh(COD)(L\text{-prolinamide})]^+$ and $[Rh(COD)(N\text{-}tert\text{-butyl-L-prolinamide})]^+$ complexes. The encapsulated catalysts were characterized by the usual spectroscopic methods, namely FTIR and XRD, and the metal content was determined by ICP.

The FTIR spectra of the zeolite, the neat complexes, the mixture of the zeolite and the neat complexes and the heterogenized samples were taken as well. The IR spectrum of the mixture of the zeolite and the $[Rh(COD)(L\text{-prolinamide})]^+$ complex was identical to the spectra of the zeolite. This indicates that the complex does not adsorb onto the outer surface of the zeolite. In the light of this observation the spectrum of the encaged catalyst shows clearly the encapsulation of the complex, because the bands of the ligand (at 2843, 2914 and 2946 cm^{-1}) also appear on the spectrum of the encapsulated sample (figure 1).

The shift of the IR bands of the bigger encapsulated complexes were observed frequently. This was interpreted to be a result of ligand distortion in the supercage. The lack of such a shift in the IR spectra indicates that the $[Rh(COD)(L\text{-prolinamide})]^+$ complex is not distorted in the supercage.

The XRD spectrum of the encapsulated sample is almost the same as that of the original Y zeolite, which supports the idea that the crystal structure of the Y zeolite did not change during the intrazeolite synthesis.

The extraction procedure removed all of the remaining complex from the zeolite surface. Thus, all the residual rhodium can be associated with the encapsulated rhodium complex. Consequently, the analysis of the rhodium content allowed the determination of the amount of the [Rh(COD)L] complex in the zeolite. On the basis of the rhodium content the concentration of the metal macrocycle was 1.17×10^{-5} mol Rh complex/g catalyst in both heterogenized catalysts.

First we have prepared the encapsulated $[Rh(COD)(L\text{-prolinamide})]^+$ complex, since the intrazeolite synthesis of this complex seemed to be easy because of the relatively small size of this complex. The synthesized homogeneous and heterogenized catalysts were active in the hydrogenation of the three alkenes. The obtained results can be seen in table 1.

There was an induction period in the case of hex-1-ene, while the cyclohexene does not show such a period. At the same time, metal precipitation was observed in the case of hex-1-ene, but this precipitation was not observed in the case of cyclohexene. The maximum rates of the homogeneous complexes were in the order hex-1-ene > cyclohexene $\gg$ 1-methylcyclohexene. The heterogenized catalysts have much higher specific activity in every case and show the activity order cyclohexene > hex-1-ene $\gg$ 1-methylcyclohexene.

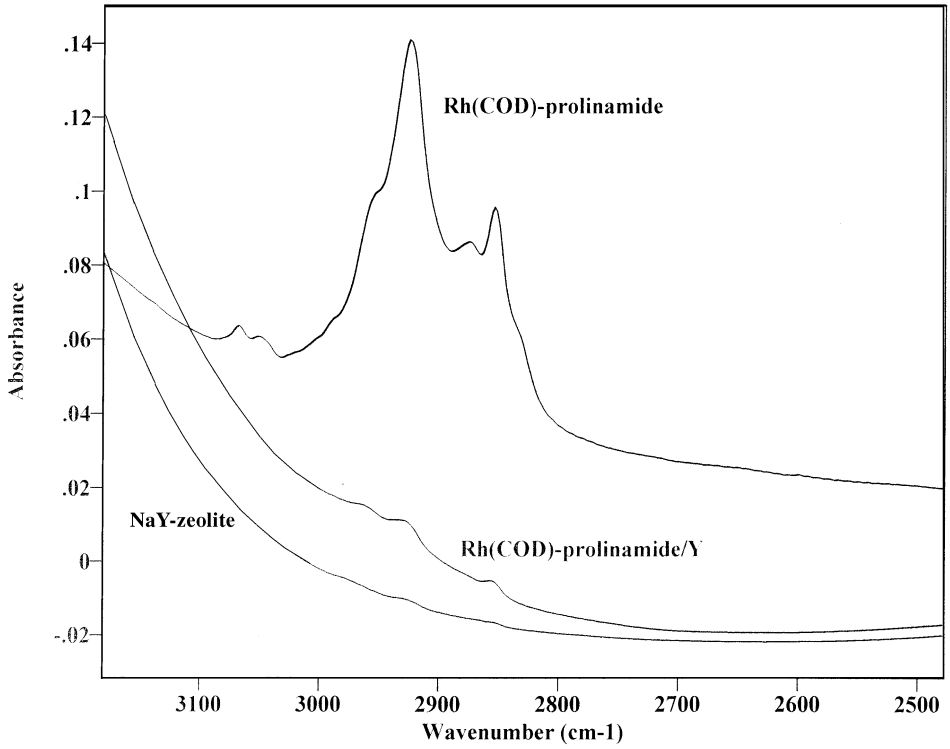

Figure 1. FTIR spectra of the zeolite, the [Rh(COD)(L-prolinamide)]$^+$ complex and the heterogenized [Rh(COD)(L-prolinamide)]$^+$/NaY catalyst.

Table 1
Conversion and specific activity (mol product/(mol rhodium complex per hour)) values for the hydrogenation of different alkenes on homogeneous and heterogenized [Rh(COD)(L-prolinamide)]$^+$ complexes.

Starting materials	Catalyst	Conversions at		Specific activities at	
		2 h	4 h	2 h	4 h
Cyclohexene	[Rh(COD)L]$^+$	36.5	69.3	58.5	52.5
Cyclohexene	[Rh(COD)L]$^+$/NaY	45.5	94.8	765.0	829.0
Hex-1-ene	[Rh(COD)L]$^+$	16.9	84.7	21.9	88.0
Hex-1-ene	[Rh(COD)L]$^+$/NaY	10.3	25.1	140.0	202.0
1-Methylcyclohexene	[Rh(COD)L]$^+$	0.2	1.2	0.26	1.4
1-Methylcyclohexene	[Rh(COD)L]$^+$/NaY	0.31	0.54	4.5	3.0

We have synthesized the [Rh(COD)(*N-tert*-butyl-L-prolinamide)]$^+$ complex, too. The FTIR spectrum shows that encapsulation of the higher *N-tert*-butyl-L-prolinamide complex has also occurred. The results of the hydrogenation reactions on homogeneous and heterogenized catalysts can be seen in table 2.

Corma and coworkers [6] prepared a similar catalyst, but in which the complex was anchored to the surface by

Table 2
Conversion and specific activity (mol product/(mol rhodium complex per hour)) values for the hydrogenation of different alkenes on homogeneous and heterogenized [Rh(COD)(*N-tert*-butyl-L-prolinamide)]$^+$ complexes.

Starting materials	Catalyst	Conversions at		Specific activities at	
		3 h	6 h	3 h	6 h
Cyclohexene	[Rh(COD)L]$^+$	11.8	17.5	14.8	7.2
Cyclohexene	[Rh(COD)L]$^+$/NaY	39.0	70.3	1089.0	515.0
Hex-1-ene	[Rh(COD)L]$^+$	39.3	90.7	40.0	52.3
Hex-1-ene	[Rh(COD)L]$^+$/NaY	3.8	16.9	807.0	1315.0
1-Methylcyclohexene	[Rh(COD)L]$^+$	59.5	73.8	64.0	15.3
1-Methylcyclohexene	[Rh(COD)L]$^+$/NaY	0.75	2.3	36.0	75.0

Table 3
Hex-1-ene/cyclohexene rate ratio values on different catalysts.

Catalyst	Hex-1-ene/cyclohexene rate ratio values
[Rh(COD)(L-prolinamide)]$^+$	0.37
[Rh(COD)(L-prolinamide)]$^+$/NaY	0.18
[Rh(COD)(*N-tert*-butyl-L-prolinamide)]$^+$	2.7
[Rh(COD)(*N-tert*-butyl-L-prolinamide)]$^+$/NaY	0.74

a covalent bond. This catalyst was studied in the same hydrogenation reactions and similar specific activity values (*e.g.*, 720 mol product/(mol rhodium complex per hour) for the hydrogenation of cyclohexene) were found. In this case there was also an induction period only in the case of hex-1-ene. The maximum rates of the homogeneous complexes were in the order 1-methylcyclohexene > hex-1-ene > cyclohexene. The initial specific rates on the heterogenized catalysts were also much higher than on the homogeneous ones, except for the hydrogenation of 1-methylcyclohexene, where this rate was lower. This fact indicates that the hydrogenation occurs in the supercage and the intraparticle diffusion of the relatively large 1-methylcyclohexene molecule is difficult. The hex-1-ene/cyclohexene hydrogenation ratio values can be seen in table 3. On the anchored catalyst Corma found that the ratio was higher than 1 on all catalysts [6]. We have found, however, only one catalyst which had the same value, and the other three catalysts showed a ratio lower than 1.

Both heterogenized catalysts were used in subsequent catalytic runs without any decrease of the catalytic activity.

(*Z*)-methyl-(2-acetamido-3-phenylacrylate) was used as a substrate to measure the efficiency of the [Rh(COD)(*N-tert*-butyl-L-prolinamide)]$^+$ and [Rh(COD)(*N-tert*-butyl-L-prolinamide)]$^+$/NaY complexes as enantioselective hydrogenation catalysts. Homogeneous hydrogenation in butan-2-one gave only 3% ee, while the heterogenized catalyst showed 20% ee.

References

[1] G.W. Parshall and S.D. Ittel, *Homogeneous Catalysis*, 2nd edition (Wiley-Interscience, 1992).
[2] F.R. Hartley, *Supported Metal Complexes* (Reidel, Dordrecht, 1985).
[3] M. Eisen, T. Bernstein, J. Blumm and H. Schumann, J. Mol. Catal. 43 (1987) 199.
[4] R.V. Parish, D. Habibi and V. Mohammadi, J. Organometall. Chem. 369 (1989) 17.
[5] H. Brunner, E. Bieldmeier and J. Wiehl, J. Organometall. Chem. 384 (1990) 223.
[6] F. Sánchez, M. Iglesias, A. Corma and C. del Pino, J. Mol. Catal. 70 (1991) 369.
[7] A. Carmona, A. Corma, M. Iglesias, A. San José and F. Sánchez, J. Organometall. Chem. 492 (1995) 11.
[8] A. Corma, M. Isabel de Dios, M. Iglesias and F. Sánchez, Stud. Surf. Sci. Catal. 108 (1997) 501.
[9] G. Gbery, Á. Zsigmond and K.J. Balkus, Catal. Lett. 74 (2001) 77.
[10] R.A. Sheldon, I.W.C.E. Arends and H.E.B. Lempers, Catal. Today 41 (1998) 387.
[11] G.V. Smith and F. Notheisz, *Heterogeneous Catalysis in Organic Chemistry* (Academic Press, San Diego, 1999), p. 252.