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Comparative study of "ship-in-a-bottle" and anchored heterogenized Rh complexes

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Abstract

Heterogenized rhodium complexes were prepared by two different methods ("ship-in-a-bottle" and anchoring methods) and the catalysts were used in the hydrogenation of simple and prochiral alkenes. The "ship-in-a-bottle" type heterogenized rhodium complexes were active in the hydrogenation of hex-1-ene, cyclohexene, and 1-methylcyclohexene. At the same time the heterogenized catalyst had all the expected advantages of the heterogeneous system, namely easy handling and recyclability. The anchored catalyst could also catalyze the same hydrogenation reactions and showed all the advantages of the heterogeneous catalysts. However, the latter one was much more active in the above hydrogenation reactions than the "ship-in-a-bottle" type catalysts. Moreover, the anchored catalyst showed higher *ee* in the enantioselective hydrogenation of *trans*-2-methylpent-2-enoic acid than its encapsulated counterpart.
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Keywords: Olefin hydrogenation; Anchored catalysts; Heterogenized Rh complexes; Encapsulated catalysts

1. Introduction

Recently, enantioselective hydrogenations with soluble chiral catalysts have become more and more important in the pharmaceutical industry, and consequently in catalytic research as well. Since heterogeneous catalysts have several advantages over soluble catalysts, an increased demand has developed for the heterogenization of homogeneous complexes [1–3].

Several different methods have been introduced to heterogenize homogeneous complexes using organic and inorganic supports [4–6]. Among the more interesting supports are the molecular sieves. Their three-dimensional channel systems may provide site isolation as well as size and shape selectivity. Complexes entrapped in zeolite pores, but not necessarily bound to the surface, are often referred as "ship-in-a-bottle" complexes [7].

A new method of heterogenizing homogeneous hydrogenation catalysts has recently been introduced by Augustine and co-workers [8a]. With this method the homogeneous complex can be anchored to different support materials, resulting in a catalyst which is at least as active as the homogeneous one, as well as having the advantages of a heterogeneous system. This method involves the attachment of the metal complex to a solid support using a heteropoly acid as an anchoring agent. The heteropoly acid is attached to the support by the interaction of the acidic protons with the basic sites of the support. Either ion pairing or a direct bond between oxygen atoms of the heteropoly acid and the metal has been proposed to account for the heterogenization of the metal complex [8b].

Recently we have prepared a series of $[Rh(COD)L]^+$ complexes, where L = L-prolinamide or *N-tert*-butyl-L-prolinamide, and their encapsulated analogues [9]. The hydrogenation of several different alkenes, hex-1-ene, cyclohexene, and 1-methylcyclohexene, was studied on these heterogenized samples. The heterogenized catalysts were active in these hydrogenation reactions and showed higher specific activity than their homogeneous counterparts. In the enantioselective hydrogenation of (*Z*)-methyl-α-acetamidocinnamate the observed *ee* values using the encapsulated catalysts were higher than in the case of the homogenous analogues. The improvement in stereoselectivity could be a consequence of steric constraints imposed by supercage dimensions. At the same time, the encapsulated

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catalysts had all the advantages of a heterogenized system: easy of recovery and recycling.

In this paper we want to publish a comparative study of heterogenized catalysts prepared by two different methods, namely the "ship-in-a-bottle" and anchoring methods. For better comparison we have used the same protocol for both systems and the same substrates and reaction conditions.

2. Experimental methods

2.1. Synthesis of the complexes

L-prolinamide was purchased from Aldrich and the *N-tert*-butyl-L-prolinamide ligand was synthesized according to the literature [10]. For the synthesis of the complexes a solution of 78 mg (0.2 mmol) of rhodium complex precursor, $[Rh(COD)Cl]_2$ (Alfa Aesar), was deoxygenated in 20 ml of dry CH_2Cl_2 with argon, and 77.9 mg (0.4 mmol) of $AgBF_4$ was added to the mixture and stirred for 1 h under an argon atmosphere. Next 46 or 68 mg (0.4 mmol) of L-prolinamide or *N-tert*-butyl-L-prolinamide, respectively, was added to the solution and it was then stirred for 3 h to produce the $[Rh(COD)L]^+$ complex. The white precipitate (AgCl) was filtered from the yellow solution and the solvent was evaporated.

2.2. Encapsulation of the complexes

A solution of 78 mg (0.2 mmol) of the rhodium complex precursor, $[Rh(COD)Cl]_2$, was deoxygenated in 20 ml of dry CH_2Cl_2 with argon. Then 77.9 mg (0.4 mmol) of $AgBF_4$ was added to the mixture and it was stirred for 1 h under argon. The white precipitate (AgCl) was filtered and 2.0 g of NaY zeolite was added to the remaining liquid. This mixture was stirred for 3 h under argon to produce the $[Rh(COD)]^+$ exchanged zeolite. Next, 46 or 68 mg (0.4 mmol) of L-prolinamide or *N-tert*-butyl-L-prolinamide, respectively, was added to the solution and it was stirred overnight to synthesize the encapsulated $[Rh(COD)L]^+$ complexes. The catalyst was filtered and washed several times with CH_2Cl_2 to remove the surface $[Rh(COD)L]^+$ complexes. The catalysts were dried in vacuum at 373 K overnight.

2.3. Anchoring of homogeneous complexes

This type of heterogenized catalysts was prepared using the new technique for anchoring homogeneous complexes developed by Augustine and co-workers [8a]. Tungstophosphoric acid hydrate (HPA) was purchased from Merck. In 30 ml of ethanol, 1.5 g of NaY zeolite (Aldrich) was suspended. In 25 ml of ethanol, 288.0 mg (0.1 mmol) of HPA was dissolved, and this solution was dropped into the zeolite suspension with efficient stirring. The stirring was continued for 1 day. The mixture was filtered and the solid residue was suspended in 30 ml of ethanol. Then 21.7 mg (0.1 mmol) of the Rh-complex was dissolved in 10 ml of deoxygenated ethanol and this solution was dropped slowly, with stirring, into the suspension. The stirring was continued for another day. The mixture was filtered and washed with ethanol. The solid material was dried at 303 K for 2 h in vacuum and for 1 day under argon.

2.4. Catalyst characterization

The metal contents of the heterogenized (encapsulated or anchored) catalysts were determined by ICP and they were characterized by the usual spectroscopic methods FT-IR and XRD. The FT-IR spectra of the zeolite, the neat complexes, and the heterogenized samples were taken, as well. The spectra were recorded in KBr pellets, using a Bio-Rad FTS-65 A spectrophotometer, in the range 400–4000 cm^{-1}. The XRD diffractograms were recorded on a Philips PW-1830 diffractometer.

To determine the metal content the sample was dissolved in concentrated HNO_3 and HF. The metal content of these solutions was determined by JOBIN YVON 24 type ICP-AES instrument.

During the synthesis of the anchored complexes the HPA concentration in the filtrate was determined by UV spectroscopy and the amount of HPA adsorbed on the zeolite was calculated.

2.5. Hydrogenation experiments

Hex-1-ene, cyclohexene, and 1-methylcyclohexene have been hydrogenated in a batch reactor of capacity 60 ml, at reaction temperature 338 K, and hydrogen pressure 0.6 MPa. Either 10 mg of the homogeneous or 300 mg of the heterogenized catalysts were added to 5 ml of 4-methylpentan-2-one, followed by 1 ml of alkene. The reactor was pressurized by hydrogen gas and the stirring was started. Samples were taken every 2 or 3 h from the reaction mixture. The products were analyzed by capillary gas chromatography (Hitachi 263-80) using a TCEP-60 column at 308, 323, or 353 K, and only one hydrogenated product was detected in each experiment.

2.6. Enantioselective hydrogenations

Either 10 mg of the homogeneous or 100 mg of the heterogenized catalysts and *trans*-2-methylpent-2-enoic acid were added to 5 ml of butan-2-one in the batch reactor and the same procedure as indicated above was followed. The products were analyzed by gas chromatography using He as carrier gas and a 30-m Cyclodex-B column at 368 K.

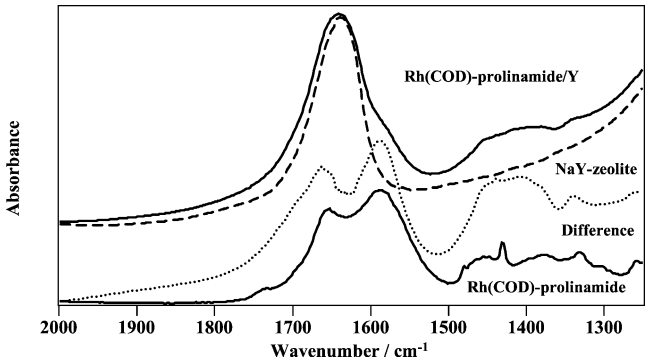

Fig. 1. FT-IR spectra of the NaY zeolite, the [Rh(COD)*N-tert*-butyl-L-prolinamide] complex, and the encapsulated [Rh(COD)*N-tert*-butyl-L-prolinamide]/NaY catalyst.

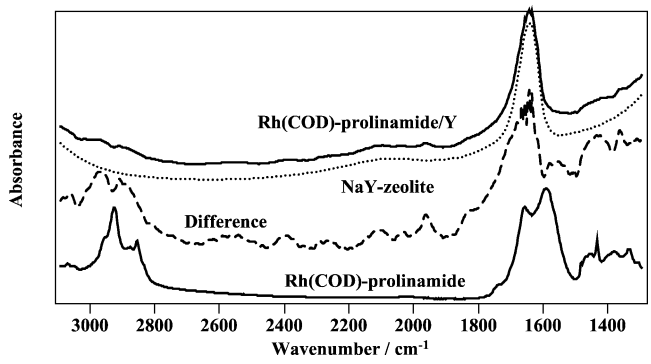

Fig. 2. FT-IR spectra of the HPA/NaY complex, the [Rh(COD)*N-tert*-butyl-L-prolinamide] complex, and the anchored [Rh(COD)*N-tert*-butyl-L-prolinamide]/HPA/NaY catalyst.

3. Results and discussion

3.1. Catalysts characterization

We have prepared the heterogenized version of [Rh(COD)(L-prolinamide)]$^+$ catalysts by two different heterogenization methods ("ship-in-a-bottle" and anchoring). The [Rh(COD)(L-prolinamide)]$^+$/NaY, [Rh(COD)(*N-tert*-butyl-L-prolinamide)]$^+$/NaY) and the anchored type ([Rh(COD)(L-prolinamide)]$^+$/HPA/NaY, [Rh(COD)(*N-tert*-butyl-L-prolinamide)]$^+$ HPA/NaY) catalysts were characterized by the usual spectroscopic methods, namely FT-IR and XRD, and the metal content was determined by ICP.

The FT-IR spectra of the zeolite, the neat [Rh(COD)*N-tert*-butyl-L-prolinamide] complex, and the encapsulated [Rh(COD)*N-tert*-butyl L-prolinamide]/NaY catalyst were taken (Fig. 1). The comparison of the two spectra (the neat complex and the encapsulated sample) showed evidence (the same bands which are characteristic of the homogeneous complex: 1680, 1590, 1340 cm^{-1}) for the encapsulation of the complex.

Since the surface complexes were removed by the extraction, this spectrum is characteristic of the encapsulated complexes. There are examples in the literature where the spectra of the encapsulated molecules are different from those of the neat complexes and this was interpreted as a result of the ligand distortion in the supercage. In Fig. 1, however, the spectra of the neat and encapsulated complexes are similar, indicating that the [Rh(COD)*N-tert*-butyl-L-prolinamide]$^+$ complex is not distorted in the supercage.

In the case of the anchored catalyst the same spectra were taken, both the neat complex and the heterogenized sample (Fig. 2). The comparison of the spectra of [Rh(COD)L-prolinamide] and [Rh(COD)*tert*-Bu-prolinamide]$^+$/NaY catalysts (Fig. 2) showed similar, but not so convincing evidence for anchoring of the complex. The reason for this could be the disturbing effect of the HPA and the lower metal complex concentration, together.

The XRD diffractograms of the encapsulated and anchored samples were compared to the diffractogram of the original zeolite to check the possible change in the zeolite structure during the synthesis (Fig. 3). We observed that the spectra of the heterogenized samples were the same as that of the original NaY zeolite, which supports the idea that the crystal structure of the NaY zeolite did not change during the intrazeolite synthesis or the anchoring process.

During the preparation process the extraction was done until a colorless extract was received. This is a generally accepted process for preparing heterogenized catalysts, but we made an additional experiment in which we prepared an impregnated catalyst, where the complex was only adsorbed on the outer surface of the zeolite. This catalyst had some activity in the hydrogenation of alkenes, but after the extraction process the catalyst prepared in this way was completely inactive in the hydrogenation reaction, showing that the adsorbed complexes can be removed completely by the extraction.

The metal content of both heterogenized samples was determined by ICP after the samples were dissolved in HNO_3 and HF. The rhodium content of the catalysts can be seen in Table 1. As we proved with an additional experiment, the extraction procedure removed the total amount of complex from the zeolite surface. Thus, all the residual rhodium can be found in the zeolite cages and may be associated with the amount of the encapsulated [Rh(COD)L]$^+$ complexes. The amount of the anchored ([Rh(COD)L]$^+$ complexes can be calculated in a similar way.

Comparing the amount of Rh complexes determined by ICP on the two catalysts, it is clear that the FT-IR spectrum is less convincing for the anchored catalyst because the amount of the complex is much less in the anchored catalysts than in the encapsulated ones.

Table 1
Rhodium contents of the encapsulated and anchored catalysts

Catalysts	mol Rh complex/g catalyst $\times 10^5$
[Rh(COD)L-prolinamide]$^+$/NaY	1.17
[Rh(COD)*N-tert*-butyl-L-prolinamide]$^+$/NaY	1.17
[Rh(COD)L-prolinamide]/HPA/NaY	0.24
[Rh(COD)*N-tert*-butyl-L-prolinamide]/HPA/NaY	0.29

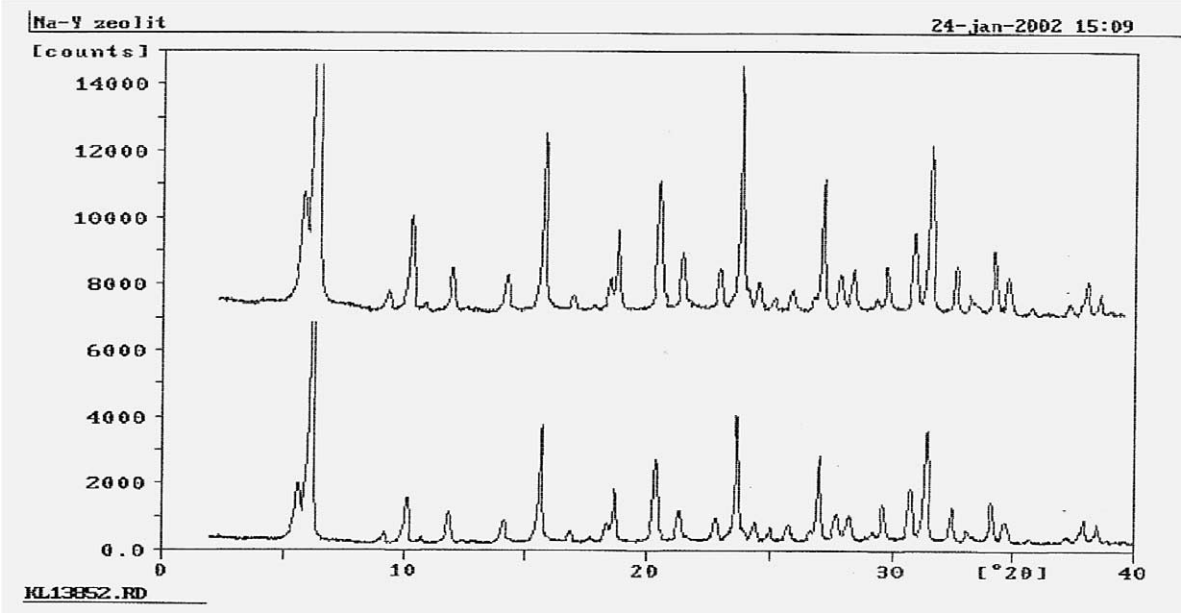

Fig. 3. XRD diffractograms of the NaY zeolite and the anchored [Rh(COD)*N-tert*-butyl-L-prolinamide] catalyst.

The amount of adsorbed HPA was determined by UV spectroscopy and it was found that the HPA content of the catalyst was 4.8×10^{-5} mol HPA/g catalyst.

3.2. Hydrogenation reactions

The encapsulated and the anchored [Rh(COD)L-prolinamide]$^+$ complexes were studied in the hydrogenation of three alkenes, namely hexe-1-ene, cyclohexene, and 1-methylcyclohexene. The activities of these catalysts were compared to those of the homogeneous reactions (Table 2).

As can be seen, both of the heterogenized catalysts were active in the above hydrogenation reactions. As a matter of fact, the heterogenized catalysts had the same conversions as the homogeneous one, or slightly higher. This feature is even more pronounced if we compare the specific activities (Table 2).

As Table 2 clearly shows, the heterogenized catalysts had higher activities than the homogeneous one. If we compare the two heterogenized catalysts we can observe that the activity of the anchored complex is higher. Depending on the studied olefin the TOF's are about 5 to 800 times higher than those observed on the encapsulated catalyst.

The fact that the heterogenized catalysts have a higher reaction rate is one of the expected advantages of using heterogenized catalysts and is in good agreement with our former results [11]. In different systems we and some other authors [12] have observed higher reaction rates on heterogenized samples. The explanation could be that in the homogeneous condition the reaction rate is decreased by the poor solubility of these complexes in most organic solvents and by self-degradation. If we eliminate these factors by heterogenizing the complex we can expect a higher reaction rate. The site isolation effect which works on the heterogenized condition may also be an explanation for the higher rate, since the complex is in a molecularly dispersed form and because of this, it is not subject to self-degradation.

Table 2
Conversion and specific activity (mol product/(mol rhodium complex · hour), values for the hydrogenation of different alkenes on homogeneous, encapsulated (NaY), and anchored (HPA/NaY) [Rh(COD)L-prolinamide]$^+$ complexes

Alkenes	Catalysts	Conversions			Initial specific activities
		1 h	2 h	3 h	
1	[Rh(COD)L]$^+$		36.5		58.5
1	[Rh(COD)L]$^+$/NaY		45.5		765
1	[Rh(COD)L]$^+$/HPA/NaY	25.44	76.94	100	3474
2	[Rh(COD)L]$^+$		16.9		27
2	[Rh(COD)L]$^+$/NaY		10.3		173
2	[Rh(COD)L]$^+$/HPA/NaY	66.74	100		7382
3	[Rh(COD)L]$^+$		0.2		0.32
3	[Rh(COD)L]$^+$/NaY		0.31		5.2
3	[Rh(COD)L]$^+$/HPA/NaY	8.7	40.75	67.65	1017

Alkenes: cyclohexene (**1**), hex-1-ene (**2**), or 1-methylcyclohexene (**3**).

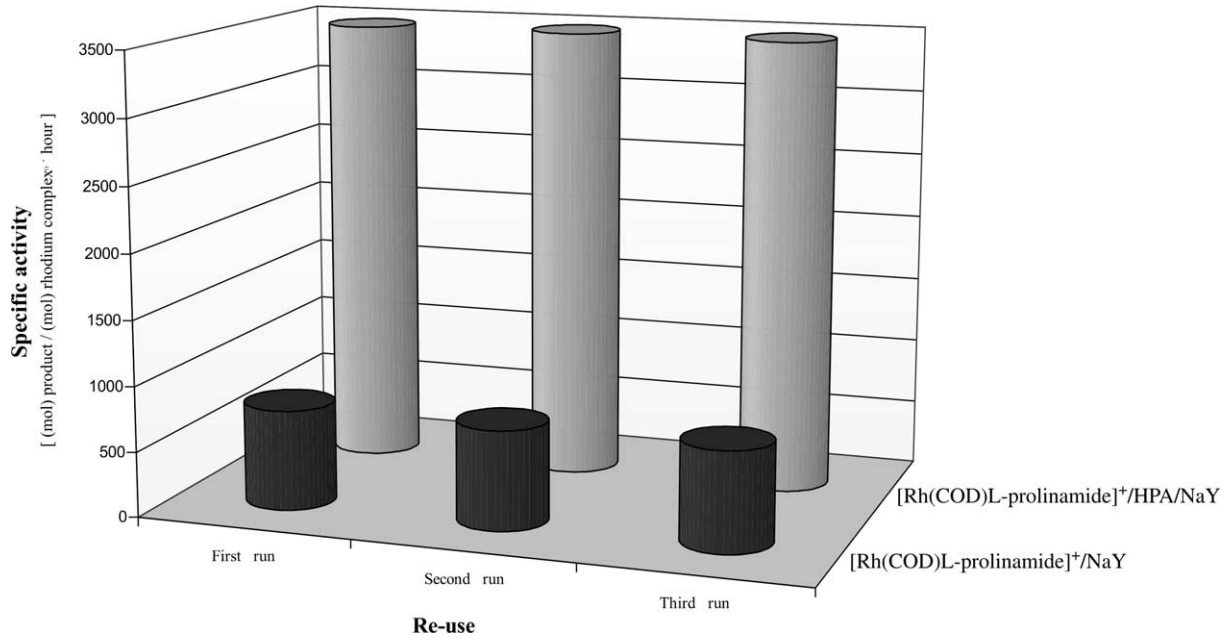

Fig. 4. The activity in the hydrogenation of cyclohexene in three subsequent runs on anchored [Rh(COD)L-prolinamide] catalysts.

However, in the case of the two heterogenized systems, the observed difference in the activity could be connected with the diffusion limitation in our opinion. In the case of the encapsulated catalyst the complex can be found inside the zeolite in the supercage, while in the case of anchored catalysts the complex is probably situated on the outer surface of the zeolite. In other words, in the case of anchored catalysts the real catalytic sites are more accessible to the reactant molecules than in the case of the encapsulated catalysts.

One of the advantages of using heterogenized catalysts is recyclability. Both the encapsulated and the anchored catalysts were used in subsequent catalytic runs without any significant decrease in the catalytic activity (Fig. 4).

The hydrogenation of the above-mentioned alkenes on the encapsulated and the anchored [Rh(COD)*N-tert*-butyl-L-prolinamide]$^+$ complexes was also studied. Results presented in Table 3 suggest the same conclusion that we have already observed on the [Rh(COD)-L-prolinamide]$^+$ catalyst and its heterogenized analogs. The heterogenized catalysts had a higher reaction rate than the homogeneous ones, which is more significant when the specific activities are compared. In our opinion the same explanation can be given as above.

3.3. Enantioselective hydrogenations

The *tert*-butyl-substituted derivatives of [Rh(COD)-L-prolinamide]$^+$ are optically active and can catalyze stereoselective hydrogenations. (*Z*)-methyl-acetamidocinnamate was our starting material for the encapsulated catalyst and we observed a lower *ee* on the homogeneous catalyst than on the heterogeneous one [9]. This finding was in good agreement with our former observations [11b] and a pos-

Table 3
Conversion and specific activity (mol product/(mol rhodium complex · hour), values for the hydrogenation of alkenes on homogeneous, encapsulated (NaY), and anchored (HPA/NaY) [Rh(COD)*N-tert*-butyl-L-prolinamide]$^+$ complexes

Alkenes	Catalysts	Conversions			Initial specific activities
		1 h	2 h	3 h	
1	[Rh(COD)L]$^+$		7.9		14.8
1	[Rh(COD)L]$^+$/NaY		12.8		1089
1	[Rh(COD)L]$^+$/HPA/NaY	61	100		7032
2	[Rh(COD)L]$^+$		26.2		49
2	[Rh(COD)L]$^+$/NaY		11.6		987
2	[Rh(COD)L]$^+$/HPA/NaY	64.5	100		6985
3	[Rh(COD)L]$^+$		39.7		74
3	[Rh(COD)L]$^+$/NaY		0.5		42.5
3	[Rh(COD)L]$^+$/HPA/NaY	37.2	75.8	95.4	3778

Alkenes: cyclohexene (**1**), hex-1-ene (**2**), or 1-methylcyclohexene (**3**).

Table 4
Enantioselective hydrogenation of *trans*-2-methylpent-2-enoic acid on [Rh(COD)*N-tert*-butyl-L-prolinamide]$^+$ / NaY and [Rh(COD)*N-tert*-butyl-L-prolinamide]/HPA/NaY complexes

Catalysts	Conversions at 1h (%)	Enantiomeric excess (%)
[Rh(COD)*N-tert*-butyl-L-prolinamide]$^+$	100	13
[Rh(COD)*N-tert*-butyl-L-prolinamide]$^+$ /NaY	100	17
[Rh(COD)*N-tert*-butyl-L-prolinamide]/HPA/NaY	100	31

sible explanation for the improved stereoselectivity is that steric constraints imposed supercage dimensions.

Trans-2-methylpent-2-enoic acid was the substrate used to study the efficiency of the encapsulated and the anchored complexes in the enantioselective hydrogenation. The obtained results can be seen in Table 4. Table 4 clearly indicates the findings that we have come to expect considering enantioselectivity. The *ee* value was higher using the encapsulated catalyst than with the homogeneous catalyst and it was higher yet with the anchored complex. In other words, not only was the specific activity of the anchored catalyst much higher than the encapsulated ones, but the enantioselectivity was higher as well.

4. Conclusions

1. We have prepared encapsulated [Rh(COD)L]$^+$ complexes, where L = L-prolinamide or *N-tert*-butyl-L-prolinamide. The hydrogenation of three simple olefins and one prochiral olefin on these catalysts were studied and higher specific activities and stereoselectivities were proven on the heterogenized catalysts.
2. The anchored [Rh(COD)L]$^+$ complexes on NaY zeolite were also prepared, where L is the same (L = L-prolinamide or *N-tert*-butyl-L-prolinamide). To our knowledge, this is the first example of preparation of this type of catalyst by this method. Similar hydrogenation reactions were studied on these new heterogenized catalysts.
3. Comparing the two heterogenized systems, we found that not only the specific activities of the anchored complexes but the enantioselectivity as well was higher than on the encapsulated catalysts. A possible explanation for these findings could be that the real catalytic sites of the anchored complexes are more accessible for the substrate material than in the encapsulated catalysts.
4. Both heterogenized systems showed all the expected advantages of the heterogeneous catalysts, namely, easy handling and the possibility of use in several subsequent runs without any significant loss of catalytic activity.

Acknowledgments

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References

[1] (a) K.J. Balkus Jr., A.E. Gabrielov, J. Inclusion Phenom. Mol. Recognition Chem. 21 (1995) 159;
(b) K.J. Balkus Jr., M. Eissa, R. Levado, J. Am. Chem. Soc. 117 (1995) 10753.
[2] M.J. Sabater, A. Corma, A. Domenech, V. Fornés, H. Garcia, J. Chem. Soc. Chem. Commun. (1997) 1285.
[3] (a) J. Blum, D. Avnir, H. Schumann, Chemtech (1999) 32;
(b) I.F.J. Vankelecom, D. Tas, R.F. Parton, V. Van de Vyver, P.A. Jacobs, Angew. Chem. Int. Ed. Engl. 35 (1996) 1346.
[4] (a) D.E. De Vos, F. Thibault-Starzyk, P.P. Knops-Gerrits, P.A. Jacobs, Macromol. Symp. 80 (1994) 157;
(b) D.E. De Vos, P.P. Knops-Gerrits, R.F. Parton, B.M. Weckhuysen, P.A. Jacobs, R.A. Schoonheydt, J. Inclusion Phenom. Mol. Recognition Chem. 21 (1995) 185.
[5] F. Bedioui, Coord. Chem. Rev. 144 (1995) 39.
[6] (a) G.V. Smith, F. Notheisz, in: Heterogeneous Catalysis in Organic Chemistry, Academic Press, San Diego, CA, 1999, p. 251;
(b) Á. Zsigmond, F. Notheisz, Z. Fráter, J.E. Bäckvall, Stud. Surf. Sci. Catal. 108 (1997) 453.
[7] R.A. Sheldon, I.W.C.E. Arends, H.E.B. Lempers, Catal. Today 41 (1998) 387.
[8] (a) R. Augustine, S. Tanielyan, S. Anderson, H. Yang, Chem. Commun. (1999) 1257;
(b) C. Bianchini, P. Barbaro, Top. Catal. 19 (2002) 17.
[9] Á. Zsigmond, K. Bogár, F. Notheisz, Catal. Lett., in press.
[10] (a) A.F. Sánchez, M. Iglesias, A. Corma, C. del Pino, J. Mol. Catal. 70 (1991) 369;
(b) A. Corma, M. Isabel de Dios, M. Iglesias, F. Sánchez, Stud. Surf. Sci. Catal. 108 (1997) 501;
(c) A. Carmona, A. Corma, M. Iglesias, A. San José, F. Sánchez, J. Organomet. Chem. 492 (1995) 11.
[11] (a) J. Wöltinger, J.E. Bäckvall, Á. Zsigmond, Eur. Chem. J. 5 (1999) 2084;
(b) G. Gbery, Á. Zsigmond, K.J. Balkus Jr., Catal. Lett. 74 (2001) 77;
(c) Á. Zsigmond, F. Notheisz, G. Csjernyik, J.E. Bäckvall, Top. Catal. 19 (2002) 119.
[12] (a) R.F. Parton, L. Uitterhoeven, P.A. Jacobs, Stud. Surf. Sci. Catal. 59 (1991) 395;
(b) R.F. Parton, C.P. Bezoukhanova, J. Grobet, P.J. Grobet, P.A. Jacobs, Stud. Surf. Sci. Catal. 83 (1994) 371.