

New Rhodium Complexes anchored on Modified USY Zeolites. A Remarkable Effect of the Support on the Enantioselectivity of Catalytic Hydrogenation of Prochiral Alkenes

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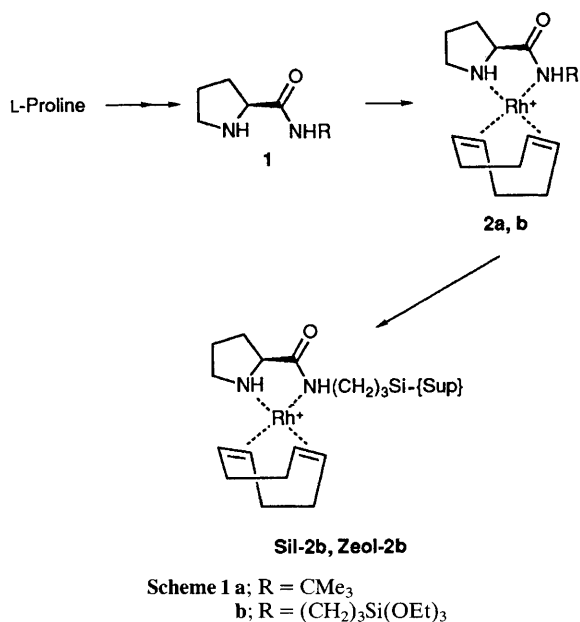
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Rh-complexes with *N*-based chiral ligands, when anchored on a modified USY-zeolite which contains profuse supermicropores, produce a remarkable increase of enantioselectivity (>95%) in the hydrogenation of *N*-acyldehydrophenylalanine derivatives and represent a truly heterogeneous counterpart of the homogeneous organometallic catalysts.

The asymmetric catalytic hydrogenation of prochiral alkenes, mainly dehydroaminoacid derivatives, constitutes one of the most impressive achievements to date in catalytic selectivity.¹ Expensive phosphorus-containing ligands and operation in homogeneous conditions are usually employed;^{2,3} there have

been only a few reports of *N*-based ligands in homogeneous form or phosphorus ones supported on different materials (silica, polymers, *etc.*) which have been shown to be usable.^{4,5} We wish to present our results on the preparation of new Rh-complexes with *N*-containing ligands, available from



proline, in solution and anchored on silica and modified USY zeolites and their application to the enantioselective hydrogenation of dehydrophenylalanine derivatives.

The new ligands **1** were prepared in three steps from L-proline, protection as *N*-carbobenzyloxy derivative, amide formation by treatment with the corresponding amine in the presence of ethyl chloroformate and triethylamine⁶ and finally deprotection using Pd/C as catalyst and cyclohexane as the hydrogen source.⁷

The cationic complexes **2a,b** were obtained, as a standard method, by Cl-bridged cleavage in the dimeric complex [RhCl(cod)]₂ (cod = cycloocta-1,5-diene) mediated by nitrogen ligands **1**, in the presence of a non-coordinative anion (hexafluorophosphate or perchlorate) in almost quantitative yields, as amorphous solids (Scheme 1).⁸

The complex **2b** was anchored to a Merck silica (particle size 63–200 μm) which was heated at 415 K under 0.01 Torr[†] for 3 h before use. Complex **2b** was also anchored to a modified USY-zeolite⁹ prepared by steam calcination at 1300 K of an 80% NH₄⁺ exchanged NaY zeolite, followed by treatment with a 0.33 mol dm⁻³ citric acid solution at 403 K, the final zeolite presented a well developed supermicropore (pore diameter 12–30 Å) system. These were formed by a controlled dealumination and destruction of the sodalite unit, which allowed direct communication between several α-cages, generating cavities wider than 12 Å.¹⁰ This dealumination process gives rise to the formation of mesopores (pore diameter > 15 Å) on the surface and in the interior of the crystallites as has been observed by transmission electron microscopy (TEM).¹¹ In our case, the steam calcination of the zeolite produces the supermicropores and mesopores which are 'cleaned' of extra framework species, which may obstruct the pores, by treatment with citric acid. The formation of supermicropores and large mesopores has been detected by N₂ adsorption-desorption (Fig. 1). At the same time a large quantity of silanol groups were obtained, as detected by IR spectroscopy, which are suitable for anchoring the complex. The unit cell size of the final zeolite was 24.40 Å, the bulk being Si/Al = 4.2, with 95% crystallinity. The zeolite was dried at 415 K under 0.01 Torr[†] before carrying out the anchoring.

The anchoring process was performed by treatment of the solid in a solution of **2b** in toluene at room temperature for

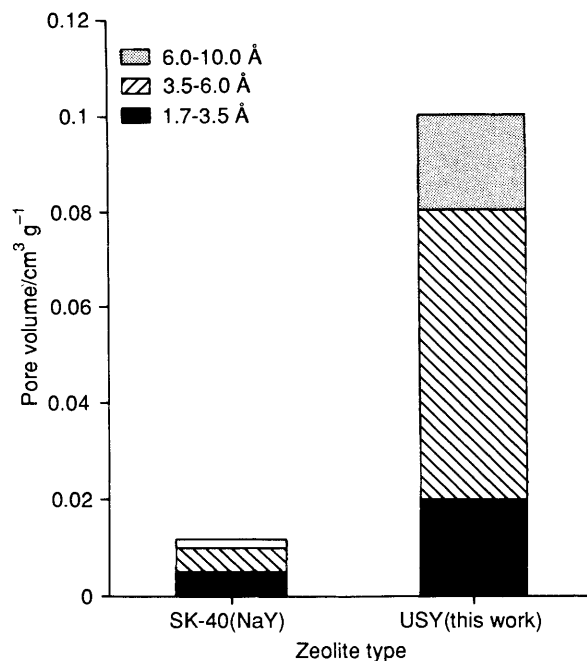


Fig. 1 Pore distribution of zeolites

Table 1 Data for catalytic hydrogenation of *N*-acylphenylalanine derivatives

Compound	Conversion/ % ^a (Time/h) ^b	Enantiomeric excess/%			Config. of 4
		2a	Sil-2b	Zeol-2b	
3a	100(10)	84.1	88.0	97.9	<i>R</i>
3b	100(14)	90.3	93.5	96.8	<i>S</i>
3c	100(10)	–	–	94.0	<i>R</i>
3d	100(10)	54.4	58.0	94.2	<i>R</i>
3e	100(12)	85.6	92.2	99.0	<i>S</i>

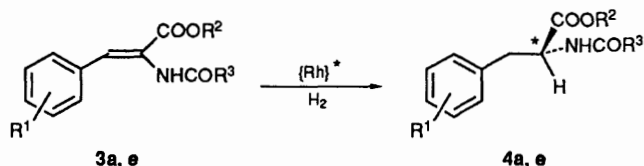
^a Measured by HPLC. ^b Using **Zeol-2b**.

24 h. It was then extracted using a Soxhlet apparatus [Cl₂CH₂-Et₂O (1:1)] and dried. The loading of metal was always 1.0 (±0.1)% wt, measured by atomic absorption of the digested samples. The soluble and immobilized catalysts are stable in air at room temperature for a long time and no special storage conditions are required. In several preparations the sequences ligand → complex → anchoring were altered without significant change in the quality of the supported catalysts obtained.

The catalysts (1:100 to 1:10000 molar amount) (**2a**, **Sil-2b**, **Zeol-2b**) were used for hydrogenation of α-acylaminocinnamate derivatives **3a–e** (Table 1) at 65 °C under 5 atm of hydrogen, in different solvents, yielding the corresponding substituted phenylalanine derivatives **4a–e** (Scheme 2) with quantitative conversion and with high enantioselectivity and low dependence on temperature and changes of hydrogen pressure.

For all the substrates tested and using the same amount of rhodium, when cationic complexes were supported on silica (**Sil-2b**), an increase in the induction period was observed (sigmoid kinetic profiles) with respect to the homogeneous catalyst **2a** (Fig. 1). On the contrary, when **2b** was supported on USY-zeolite no induction period was detected, while its activity was higher when it was used unsupported. This is probably a consequence of the concentration effect of the

[†] 1 Torr = 133.322 Pa.



Scheme 2 a; R¹ = R² = H, R³ = Me
b; R¹ = R² = H, R³ = Ph
c; R¹ = 5-OAc, 3-OMe, R² = H, R³ = Me
d; R¹ = H, R² = Et, R³ = Me
e; R¹ = H, R² = Et, R³ = Ph

zeolite and/or the interaction of the substrate due to the electrostatic fields present in the zeolite.

Moreover, the enantioselectivity is higher on the zeolite-supported complex than on either the silica-supported or unsupported complexes (Table 1), for all the substrates studied. The differences are greater for the less bulky *N*-acetyl derivatives **3a,c,d**. These facts suggest an important role for the steric constraints of the support, especially in the zeolite case where the reaction must take place in the confined spaces of the supermicropores, where the metal complexes are anchored.

The zeolite-supported catalysts were reused several times with no loss of activity or rhodium content. The increase obtained in the enantioselectivity indicates that this type of catalyst is a truly heterogeneous counterpart of homogeneous transition metal complex catalysts for the hydrogenation of prochiral alkenes.

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