Zeolite effect in the enantioselective transhydrogenation over a Co-salen “ship-in-the-bottle” complex

W. Kahlen, H.H. Wagner and W.F. Hölderich [*]

Department of Chemical Technology and Heterogeneous Catalysis, University of Technology RWTH Aachen, Worringerweg 1, 52074 Aachen, Germany
E-mail: Hoelderich@RWTH-Aachen.de

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Our investigations were focused on the transhydrogenation of carbonyl groups using Co(II)-salen complexes entrapped in zeolites. The Co-salen **1** complex was occluded in the zeolite as a “ship-in-the-bottle” (SIB) catalyst, as could be demonstrated by means of DRIFT-IR spectra, DTG, nitrogen adsorption isothermes and soxhlet extraction. The results of the test reactions show that an immobilization of the Co-salen **1** complex in the zeolite as a “SIB” complex results in an enantiomeric excess as high as in the homogeneous case. The Co-salen **1** USY SIB catalyst shows its best ee-value at higher temperature (25 °C) than the homogeneous one (−10 °C). The reason could be the steric constraints of the Co-salen complex in the zeolite framework.

Keywords: Co(II)-salen complexes, “ship-in-the-bottle” catalyst, enantioselective transhydrogenation, enantiomeric excess

1. Introduction

There are a few immobilized homogeneous enantioselective catalysts described in literature [1–3]. It is well known that (β-oxoaldiminato)cobalt(II) complexes are efficient homogeneous catalysts for enantioselective transhydrogenation of acetophenone [4]. An elegant immobilization method is the occlusion of transition metals with their organic ligands in the framework of zeolites. In such a system, also known as the “ship-in-the-bottle” (“SIB”) system, the metal–ligand complex cannot leave the zeolite framework through the windows besause of its bulkiness. Until now there are no reports on Co-salen (N,N-bis(salicylidene)-diaminocyclohexane) “SIB” catalysts which are able to catalyze an enantioselective transhydrogenation.

Our investigations are focused on the enantioselective transhydrogenation of acetophenone using Co(II)-salen complexes in a homogeneous as well as in a heterogeneous manner, i.e., entrapped in a zeolite. The influence of the immobilization of the different cobalt-salen complexes was studied, too.

2. Results and discussion

The catalyst was prepared starting from H-USY zeolite (data of the zeolite: $SiO_2/Al_2O_3 = 6$; BET = 585 m^2/g; micropore volume = 0.27 ml/g, kindly provided by Grace GmbH). After ion exchange with cobalt the different salen ligands (figure 1) were sublimated into the Co-zeolite under vacuum at 140 °C. Subsequently the zeolite was washed twice with dichloromethane to remove the metal complex which might have been deposited on the outer surface. This material was characterized by DRIFT-IR (Spektrometer 5130), XRD (Siemens D5000), ICP-AES (Spectroflame D9) and nitrogen adsorption (ASAP 2010).

2.1. Characterization

XRD showed that the structure and the crystallinity of the zeolite still remain during the preparation of the catalyst. The ICP-AES show that the Co content is 1–1.2 wt% of the zeolite. The DTG gives a hint, that the Co-salen **1** complex is in the zeolite as a “SIB” complex because the Co-salen **1** complex on SiO_2 was destroyed 50 K lower than the Co-salen **1** complex occluded in the USY zeolite.

In order to prove the presence of the Co-salen **1** complex inside the zeolite DRIFT-IR spectra of the free (a) and the occluded complex (b) were recorded and compared (figure 2). The results show that the Co-salen **1** complex is indeed present in the case of the catalyst prepared according to the “ship-in-the-bottle” approach. The non-zeolitic IR-bands at 1631, 1540, 1470 and 1447 cm^{-1} in the spectrum (b) are similar to the bands of the free complex in spectrum (a).

In figure 3 the nitrogen adsorption isotherms of the USY zeolite, the Co-salen **1** USY zeolite and the Co-salen **2** USY zeolite are presented. The micropore volumes are 0.27 cm^3/g for the parent zeolite, 0.16 cm^3/g for the Co-salen **1** USY zeolite and 0.25 cm^3/g for the Co-salen **2** USY zeolite. The BET surface areas are 585, 371 and 561 m^2/g, respectively. The Co-salen **1** USY zeolite shows a strong decrease of the micropore volume and the BET surface compared to the parent zeolite. This can be explained by the fact that the Co-salen **1** is indeed present in the microporous

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[*] To whom correspondence should be addressed.

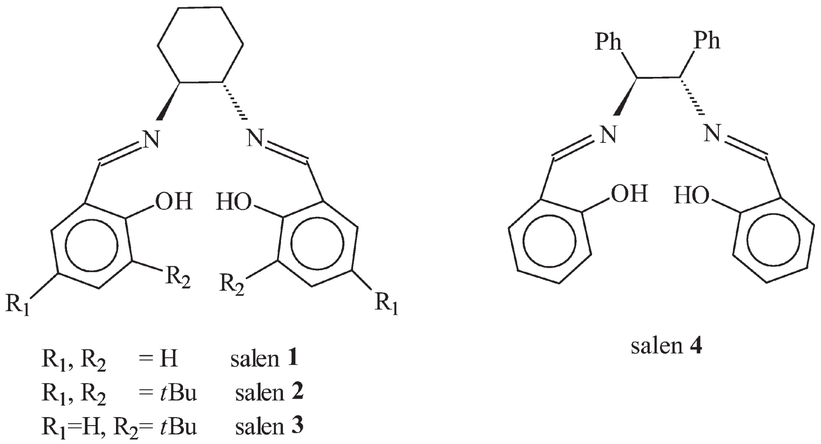

Figure 1. Different salen ligands.

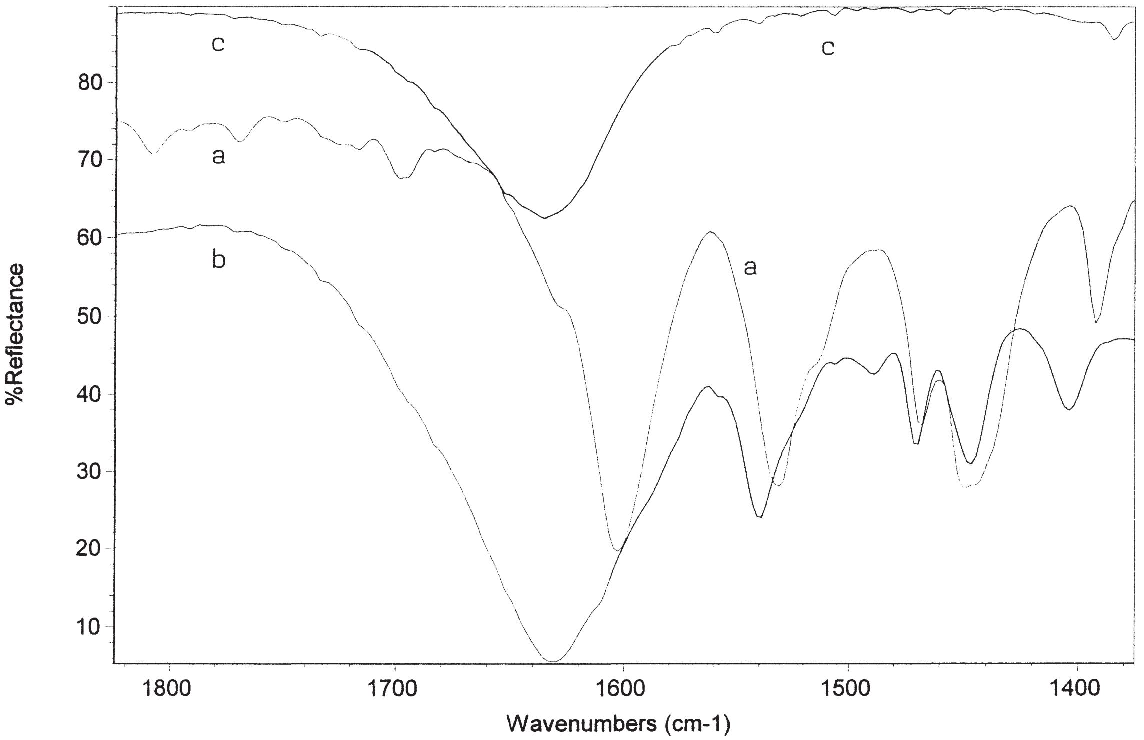

Figure 2. IR spectra of the free Co-salen **1** complex (a), the zeolite with the Co-salen **1** complex (b) and the USY zeolite (c) (transmission, KBr).

framework. In contrast, the data of nitrogen adsorption show that the BET surface area and the microporous volume of the parent zeolite and the Co-salen **2** USY zeolite are essentially the same. The much bulkier Co-salen **2** seems to be only present on the outer surface of the zeolite.

The molecular modeling also shows that only the small Co-salen **1** complex can fit in the supercage of the USY zeolite. The Co-salen **2** complex is too bulky for an occlusion in such a supercage.

Furthermore, a soxhlet extraction was done to prove whether the complex is in the zeolite as a ("SIB") catalyst. The soxhlet extraction was carried out for 24 h with CH_2Cl_2 at 40 °C. After extraction the colour of the material remains. The catalytic activity of the catalyst is also comparable before and after the extraction. This is a further hint that the Co-salen **1** complex is occluded in the zeolite supercage.

2.2. Test reactions

The transhydrogenation of acetophenone was employed as a test reaction. The hydrogenation was carried out in a batch reactor at different temperatures and times.

By using the homogeneous Co-salen **1** catalyst at –10 °C for five days a product selectivity of 99% at a conversion of 98% was obtained. The enantiomeric excess was 8%. At the higher temperature of 25 °C the selectivity was still 98% but the conversion decreased to 8% and the ee-value to 5%. The reason for the catalytic decrease is the destruction of the catalyst at higher temperatures. In contrast, the

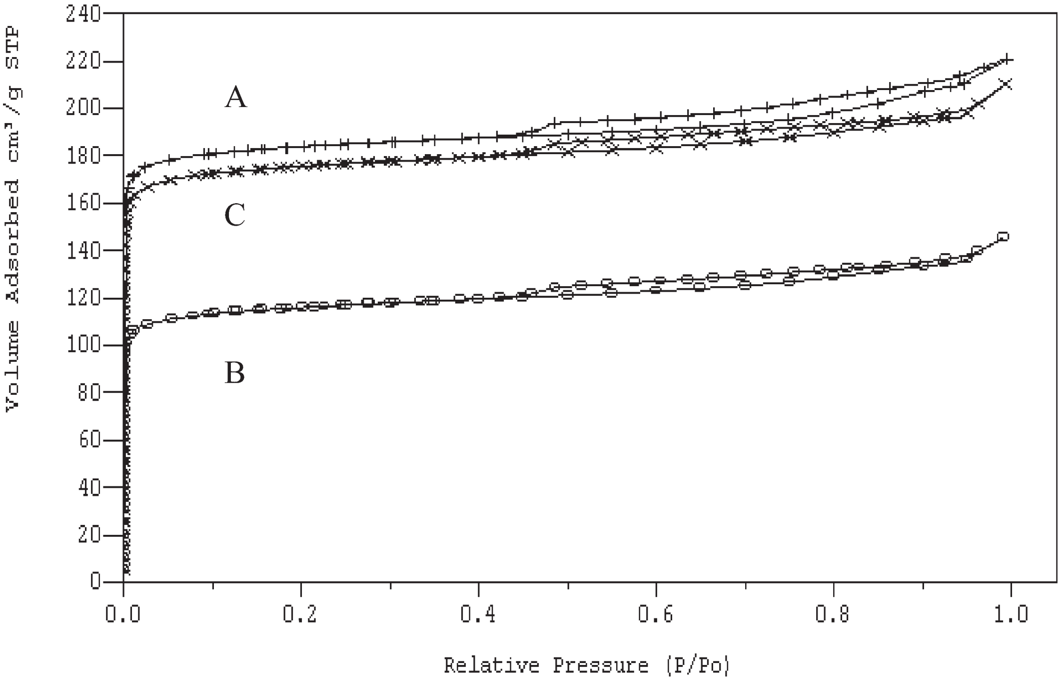

Figure 3. Isotherms of (A) USY zeolite; (B) Co-salen **1** USY zeolite; (C) Co-salen **2** USY zeolite.

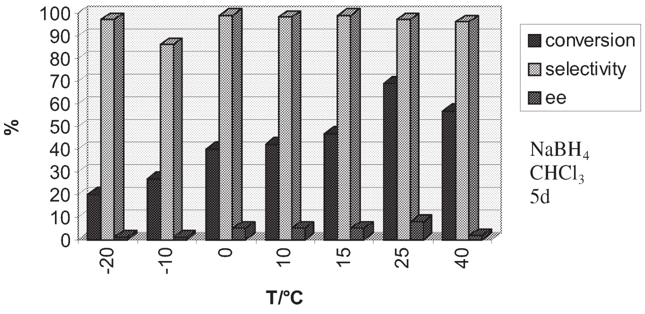

Figure 4. Catalytic results of the Co-salen **1** H-USY catalyst.

heterogeneous Co-salen **1** USY catalyst showed at –10 °C a selectivity of 97% at a conversion of 27%. The enantiomeric excess was 1.2%. The lower conversion of the immobilized Co-salen **1** complex can be caused by the diffusion effect of the zeolite. The substrates and the products have to migrate into the channels of the zeolite to approach the homogeneous catalyst.

The lower ee-value of 1.2% at −10 °C for the immobilized catalyst is understandable, because the non-catalytic transhydrogenation of acetophenone by NaBH$_4$ is more dominant. In the catalytic transhydrogenation less conversion is obtained at −10 °C than at higher temperatures. In contrast to the homogeneous catalyst the heterogeneous catalyst showed an increase of conversion and ee-value with increasing temperature. The conversion increased from 27 to 70% when the temperature increased from −10 to 25 °C, and the ee-value increased from 1.2 to 8% (figure 4).

The results of the test reactions show that an immobilization of the Co-salen **1** complex in the zeolite as a “SIB” complex results in an enantiomeric excess as high as in the homogeneous case. Furthermore, the “SIB” catalyst shows its best enantiomeric excess at a higher temperature (25 °C) than the homogeneous catalyst (−10 °C). The zeolite framework is probably responsible for this temperature effect. The steric constraints of the supercage favour a certain conformation of the Co-salen **1** complex which is needed for the enantioselective transhydrogenation. This needed conformation seems to be stable in the zeolite supercage at a temperature of 25 °C. In case of the free homogeneous complex it is necessary to lower the temperature to −10 °C in order to obtain such a conformation of the Co-salen **1** complex resulting in the same ee-value. That means the conformation of the Co-salen **1** complex suitable for enantioselective transhydrogenation is frozen at low temperature.

The location of the complex in the zeolite micropores is confirmed by the comparison of the “SIB” catalyst with amorphous aluminosilicate, impregnated with the corresponding Co-salen **1** complex. The complex leaches completely as indicated by the green colour of the resulting reaction solution. The pure white carrier is recovered. That result elucidates that the catalyst is not stable under reaction conditions. The experimental results of the transhydrogenation reaction are similar to those obtained in homogeneous reaction.

Reaction times shorter than 5 days resulted for the heterogeneous Co-salen **1** H-USY catalyst in a lower conversion. After a reaction time of 12 h 25% of conversion was obtained. After 1 day the conversion reached 35% and after 3 days 52%. The selectivity of phenylethanol was always up to 94% and the ee-value about 8%. These results indicated that a reaction time of 5 days is necessary to get a conversion higher than 60%. Reaction times higher than 5 days were not checked, because

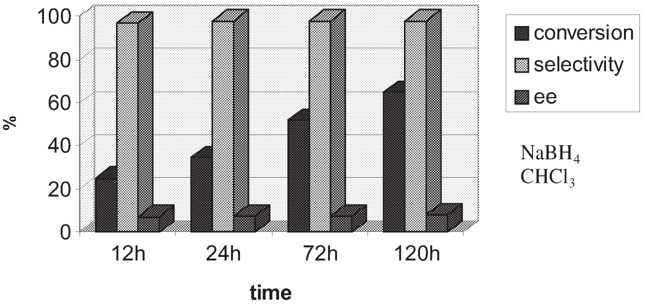

Figure 5. Different reaction times of the heterogeneous Co-salen **1** H-USY catalyst.

the conversion seemed to increase very slowly after 5 days.

Due to the high sensitivity of the catalyst against air, it shows substantial loss of performance when recycled. The highly dispersed powder is separated by centrifuging the reaction solution, in this procedure oxygen cannot completely be excluded for experimental reasons. The results show a decrease of conversion from 60 to 27% of the recycled catalyst. The enantioselectivity drops from 7.1% of the original catalyst to 2% of the corresponding recycled one. This effect is caused by decomposition of the complex when it is exposed to oxygen. Leaching of the catalyst has not been observed.

The larger Co-salen **2** complex was also tested in the transhydrogenation of acetophenone to 1-phenylethanol. Thereby the homogeneous Co-salen **2** catalyst showed at $-10\,^{\circ}$C a selectivity of 95% at a conversion of 98%. The ee-value was 20%. By increasing the temperature from -10 to $25\,^{\circ}$C the selectivity remained but the conversion decreased from 98 to 8%. The ee-value stayed at the same level of about 20%. The decrease of the conversion was possibly caused by a destruction of the catalyst at higher temperatures. When using the heterogenized Co-salen **2** catalyst at $-10\,^{\circ}$C a selectivity of 98% at a converion of 30% was obtained. The enantiomeric excess was 3%. By increasing the temperature from -10 to $25\,^{\circ}$C the conversion increased to 55%, but the ee-value was lost. So the immobilization of the larger Co-salen **2** complex on the outer surface of the zeolite resulted in a smaller enantiomeric excess than in the case of the comparable homogeneous catalyst. The fact that the Co-salen **2** complex was on the outer surface of the zeolite was shown by DTG, nitrogen adsorption and molecular modeling. A reason for this situation could be that the zeolite shelters the side of the Co-salen **2** complex which is necessary for the enantioselective transhydrogenation. In this case there are no steric constraints of the supercage which would produce a certain conformation of the Co-salen **2** complex needed for the enantioselective transhydrogenation.

These results showed that only the immobilization of the complex as a "ship-in-the-bottle" complex resulted in an enantiomeric excess as high as the comparable homogeneous one. However, it was not possible to immobilize this large Co-salen **2** catalyst in the zeolite.

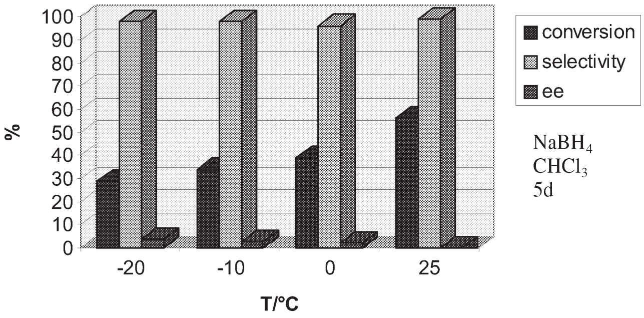

Figure 6. Catalytic results of the Co-salen **2** H-USY catalyst.

Table 1
Catalytic results of the Co-salen **3** and **4** catalysts.

Catalyst	T (°C)	Conversion (%)	Selectivity (%)	ee-value (%)
Co-salen **3** (hom)	-10	99	99	22
Co-salen **3** (hom)	25	48	99	22
Co-salen **3**/H-USY	-10	19	99	2
Co-salen **3**/H-USY	25	44	99	0
Co-salen **4** (hom)	-10	99	99	21
Co-salen **4** (hom)	25	67	99	9
Co-salen **4**/H-USY	-10	35	99	3
Co-salen **4**/H-USY	25	71	99	2

The homogeneous Co-salen **3** and **4** complexes showed at $-10\,^{\circ}$C a selectivity of 99% at a conversion of 99% and an ee-value of about 22%. At the higher temperature of $25\,^{\circ}$C the conversion decreased for both of them (table 1). The immobilization of the Co-salen **3** complex on the outer surface of the zeolite gave a selectivity of 99% at a conversion of 19% and an ee-value of 2%. The Co-salen **4** complex reached a selectivity of 99% at a conversion of 35% and an enantiomeric excess of 3% at $-10\,^{\circ}$C.

By increasing the temperature to $25\,^{\circ}$C the ee-value decreased for the Co-salen **3** complex to 0% and for the Co-salen **4** complex to 2%. These results confirm that an immobilization of larger Co-salen complexes on the outer surface of the zeolite gave less enantiomeric excess than in the comparable homogeneous case. Only in case of the immobilization of the small Co-salen **1** complex as a "SIB" complex was an ee-value achieved as high as the comparable homogeneous one.

3. Experimental

The preparation of the Co-salen **1** USY catalyst is essentially the same as described in literature for a Pt-salen USY catalyst [6]. A USY zeolite (kindly provided by Grace GmbH, $SiO_2/Al_2O_3 = 6$; BET $= 585$ m^2/g; micropore volume $= 0.27$ cm^3/g) was chosen as the carrier. 1 g zeolite was stirred for 24 h at $80\,^{\circ}$C with a solution of 0.1 g $Co(NO_3)_2$ in 5 ml water. Then 0.0023 mol of the salen ligand (salen **1**, **2**, **3**, **4**) was sublimated into the dried Co-zeolite under vacuum at $140\,^{\circ}$C. Subsequently the zeolite was washed twice with dichloromethane to remove the metal complex which might have been deposited on the outer surface. The soxhlet extraction was carried out for 24 h with CH_2Cl_2 at 40 °C.

As a test reaction the transhydrogenation of acetophenone was employed. In a standard experiment 90 mg $NaBH_4$ in 15 ml $CHCl_3$ and 0.75 ml EtOH were stirred for 1 h at 20 °C. Then the temperature of the mixture was adjusted at chosen −10, 0, 25, 40 °C. The catalyst was added (200 mg of heterogeneous Co-salen USY zeolite which corresponds to 0.042 mol indicated by ICP-AES, or 0.068 mol of homogeneous Co-salen complex) and 30 min later the substrate was added, too. After the reaction times the transhydrogenation was stopped by adding 6 ml 1 N HCl. A reaction time of 5 days was considered to be the optimum; shorter times resulted in lower yields. After neutralization with $NaHCO_3$, extraction with ether and drying over $NaSO_4$ the product was destilled and analyzed by GC (column 25 m FFAP and β1 cyclodextrin).

4. Conclusion

The Co-salen **1** complex was occluded in a USY zeolite as a “SIB” catalyst. That could be demonstrated by means of DTG, nitrogen adsorption isotherms and soxhlet extraction.

The results of the test reactions show that an immobilization of the Co-salen **1** complex in the zeolite results in an enantiomeric excess as high as over the homogeneous catalysts. Furthermore, the “SIB” catalyst shows the best enantiomeric excess, even at a higher temperature (25 °C) than the homogeneous catalyst (−10 °C). The zeolite framework seems to be responsible for this temperature effect. It could be that the steric constraints of the supercage cause a certain conformation of the Co-salen **1** complex which is necessary for the enantioselective transhydrogenation. This conformation also seems to be stabilized in the zeolite framework even at higher temperatures (25 °C). In contrast, in the homogeneous case it is important to lower the temperature to obtain this conformation of the Co-salen **1** complex to achieve the same ee-value.

The immobilization of the larger Co-salen complexes is only possible on the outer surface of the zeolite, because the complexes are too bulky to fit in the supercage of the zeolite. The transhydrogenations of these catalysts result in smaller enantiomeric excess than in the presence of the comparable homogeneous catalysts.

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