Demonstration of a zeolite effect on an encapsulated Co-salen-complex

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Abstract

In a transhydrogenation, acetophenone was converted to 1-phenylethanol over a Co(II)-salen-complex entrapped in a USY-zeolite. This catalyst was prepared via "ship in the bottle"-method. The hydrogenation in the presence of this immobilized Co(II)-salen-complex results in an enantiomeric excess as high as obtained over the homogeneous complex. High e.e.-values were obtained over the immobilized catalyst at higher temperatures (25 °C) than for the homogeneous system (−10 °C). From these experimental results, it is assumed that the zeolite favors a certain structure of the occluded salen-complex and preserves this conformations at elevated temperatures. By computer simulation, it could be illustrated that due to the interaction of the homogeneous catalyst with the zeolite the complex prefers a distorted conformation. This conformation is preserved in course of the simulations at different temperature, i.e. the probabilities of finding the observed angles inside a given interval around the most probable angle are higher for the occluded complex than for the free one.
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1. Introduction

There are a few immobilized homogeneous enantioselective/stereoselective catalysts described in the literature [1–6]. It is well known that (β-oxoaldiminato) Co(II)-complexes are efficient homogeneous catalyst for the enantioselective transhydrogenation of acetophenone [7]. Recently, we have been able to synthesize such a Co(II)-complex in the cavity of a USY-zeolite [4]. This was only possible for the Co(II)-salen-1-complex with (R,R)-(N,N′)-bis(salicylidene)-1,

2-cyclohexanediamine as ligand but not for the Co(II)-salen-2-complex with (R,R)-(N,N′)-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine as ligand (Fig. 1).

At 25 °C the occluded Co(II)-salen-1-complex showed in the investigated transhydrogenation reaction an enantioselective excess as high as in the case of the homogeneous counterpart at −10 °C [4]. Such a zeolite effect was very surprising. It was assumed that a certain conformation of the Co(II)-salen-1-complex was necessary for the achievement of the enantioselective results found in the experiments.

Investigations by means of computer simulations [5] and XRD, DRIFT, nitrogen adsorption isotherms together with ICP-AES show that the

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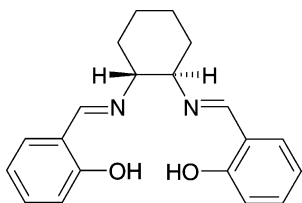*E-mail address:* hoelderich@rwth-aachen.de (W.F. Hölderich).

Fig. 1. Salen-ligand used for the encapsulation and dynamic simulation.

Co(II)-salen-1-complex has enough space and is occluded inside the zeolite framework.

In the present work, we want to use molecular dynamics simulation as a tool to demonstrate the influence of the zeolite on the conformation of the encapsulated Co(II)-salen-1-complex at different temperatures.

2. Results and discussion

2.1. Catalyst preparation and catalytic reactions

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 (Fig. 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 [4,6,7].

The enantioselective transhydrogenation of acetophenone was done with $NaBH_4$ in chloroform/ethanol mixture. The reaction was carried out for 5 days under inert gas conditions with the heterogeneous and homogeneous catalyst. The results are given in Figs. 2 and 3, respectively [8].

2.2. Computer simulation

2.2.1. The model

As a result of molecular dynamic simulations one calculates an arbitrary number of conformations from which the statistical distribution of the observed coordinates can be evaluated.

Because an ideal zeolite is a infinite periodical matrix and the movement of the atoms of the zeolite matrix during the dynamics simulations compared with the atoms of the encapsulated Co-salen-complex is
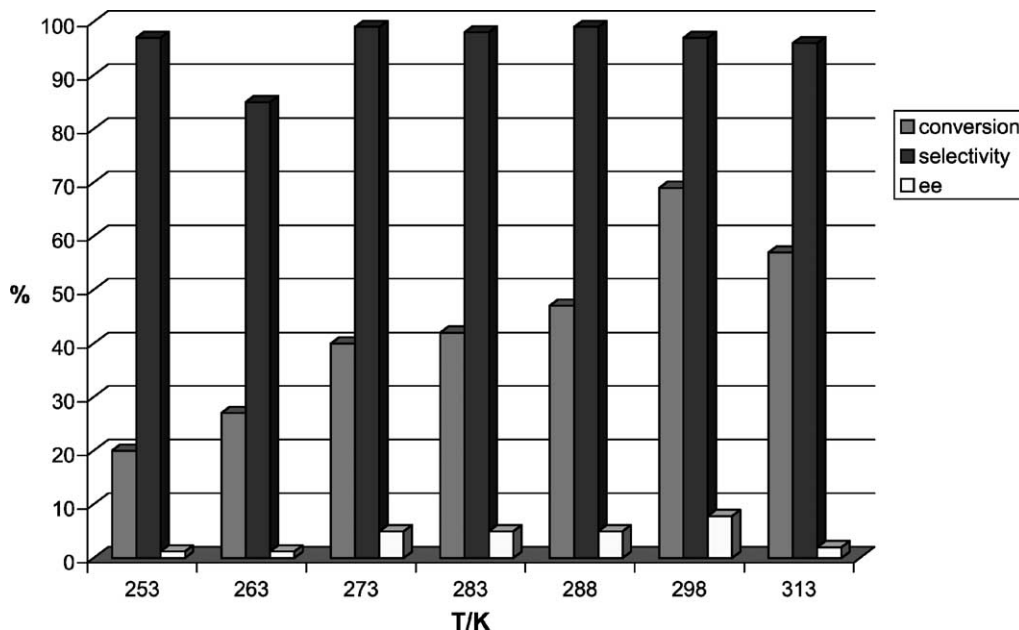

Fig. 2. Transhydrogenation of acetophenone at different temperatures with the immobilized Co-salen-1-complex.
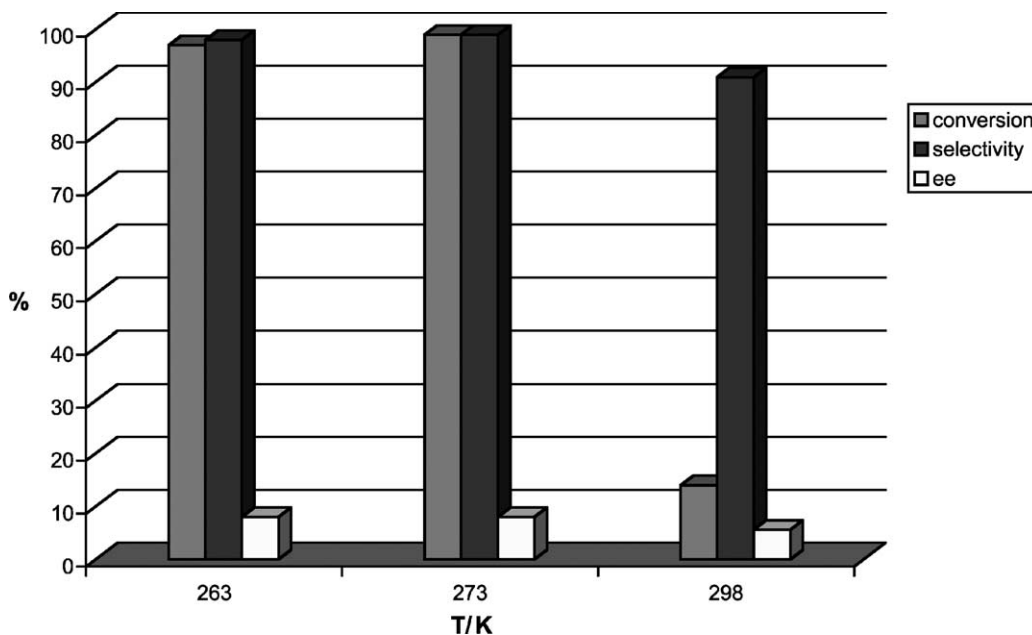
Fig. 3. Transhydrogenation of acetophenone at different temperatures with the homogeneous Co-salen-1-complex.

small, it is reasonable to assume a rigid zeolite matrix during the dynamic calculations. Furthermore, the infinite matrix is approximated by a finite sphere with a diameter of 50 Å. The bonding and non-bonding parameters of the encapsulated complex are adjusted, so that the interaction reduce to zero before the border of the sphere is reached. Besides that the calculations were performed with a purely siliceous zeolite structure [9].

Energy minimization and molecular dynamics calculations employed the Discover program by Accelrys [10]. The potential parameters were taken from the ESFF forcefield (extensible and systematic forcefield), whose parameterization is sufficient to predict the geometry of metalorganic compounds.

2.2.2. The simulation

The simulations were performed in three steps. First, a uniform starting structure for the dynamic simulations at different temperatures was generated. In the center of the 50 Å all silica zeolite sphere a Co-salen-1-complex was placed. The conformation of the salen-complex results from a simulated annealing procedure [11], where the complex undergoes a dynamic simulation at 1000 K for 50 ps directly followed by stepwise cooling to 200 K. At each cooling step, a dynamics simulation was performed for 4 ps. The step width is 100 K. At the end of the cooling procedure, the conformation of the molecule was minimized with respect to its total energy.

The conformation obtained by this procedure is used as the starting structure for the dynamic simulations at the corresponding temperature. Before data acquisition was started, the structure was equilibrated for 250 ps at the corresponding simulation temperature, so that the salen-complex fulfills the random-walk criteria during the registration period [12].

After equilibration, the atomic coordinates of the salen-complex are stored after every dynamic step for 10 ps, resulting in 10,000 structures.

2.2.3. The evaluation

The starting structure of the Co-salen-complex for the dynamic simulations after simulated annealing is given in Fig. 4.

To describe the movement of the salen-complex it is suitable to define a molecule fixed geometry, which is given by the plane through the atoms N, N_1 and CO or OH, CO and O (Fig. 4). Due to the discussed epoxidation mechanisms [13–15] the movement of
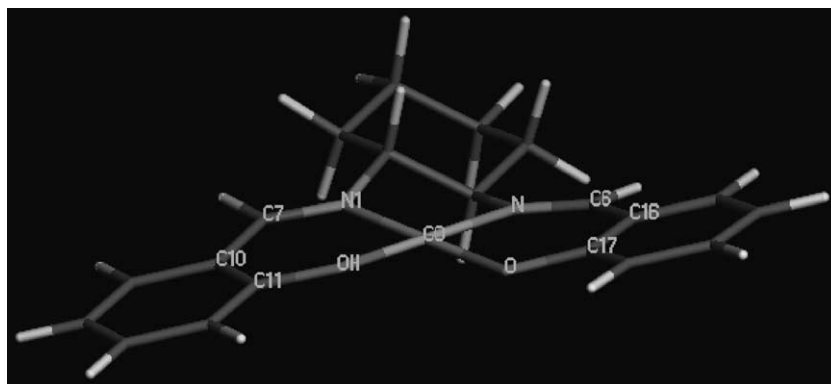
Fig. 4. Conformation of the encapsulated Co-salen-complex after the simulated annealing procedure. Additionally, the names of the atoms for calculating the observables are given.

the salen-complex during the simulations can be divided in three different categories. The swinging of the cyclohexyl substituent over and under the fixed plane is important for the approach of the substrate from the chiral backbone. The twisting motion of the phenyl-ligands, especially if 3,3′-substituted, determines the rate of approaching substrate molecules coming from the opposite site. The swinging of the phenyl-groups over and under the reference plane blocks the approach of the substrate coming from the direction of the phenyl-groups.

2.2.4. Definition and calculation of the observed coordinates

When evaluating the observed coordinates we assume, that the out of plane movements of the phenyl-groups are small compared to the dihedral angle of the twisting motion, so that the twisting motion can be described by the dihedral angle between the atoms C_{11}, C_{10}, C_7 and N_1 as well as between the atoms C_{17}, C_{16}, C_6 and N. For every calculated angles, a sign is evaluated, relative to the starting structure of the dynamic simulation.

The description of the movement of the phenyl-groups over and under the reference plane OH–CO–O is done by the angle between the reference plane and the atoms C_{17} and C_{11}, respectively. Just like for the dihedral angle a sign for the calculated angles is evaluated.

For the observation of the vibration of the cyclohexyl backbone, the distances of the carbon atoms from the plane given by the atoms N, CO and N_1 are

calculated. The sign of the calculated values determines, whether the carbon atoms lie above or below the reference plane.

2.2.5. Statistics of the observed coordinates

For the statistics the probabilities of finding a value x inside an interval $x + \Delta x$ are plotted against the value x. To the thus calculated curves Gauss-functions of the form given in Eq. (1) are fitted by a least-squares procedure:

$$F(x) = \sum_i C_i \sqrt{\frac{\alpha_i}{\pi}} \exp[-\alpha_i(x - a_i)^2] \qquad (1)$$

In the case of $i > 1$, it was made sure that the free widths at half height (FWHH) of the individual Gauss-functions were in the same range. As an example of such a procedure the calculated distribution together with the fitted Gauss functions are given in Fig. 5.

2.2.6. Comparison of the motion of the Co-salen-complex inside and outside the zeolite matrix

The results of the simulation and fitting procedures are given in Table 1 in form of the most probable dihedral and swing angles representing the motions of the phenyl-groups.

The values of the homogeneous complex represent clearly the C_2-symmetry of the Co-salen-complex. On the contrary, there is a remarkable deviation from C_2-symmetry in the encapsulated complex. Except
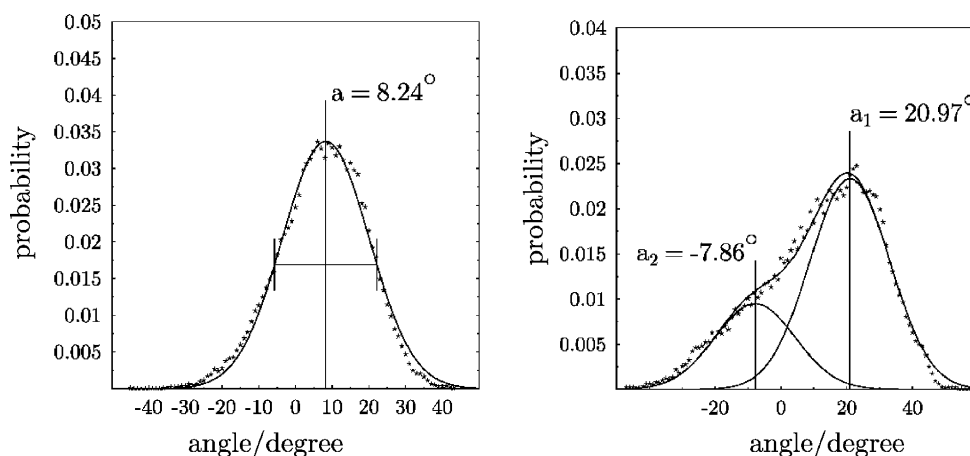
Fig. 5. Simulated probability distributions of the occluded complex describing the torsion of the phenyl-group between the atoms C_{11}, C_{10}, C_7 and N_1 (above) and the its swinging above and below the reference plane given by OH, CO and O. The calculation was performed at 300 K. The solid line represents the fit of Eq. (1) by the least-squares method.

for the results at 290 K, this deviation shows in the same direction. From geometric considerations, it is obvious that due to this distortion one side of the encapsulated complex is more shielded by the phenyl-ligands than the other.

Furthermore, the probability of finding an angle inside an interval around the most probable angle was calculated. The aim is to find out whether a special conformation is favored inside or outside the zeolite. These probabilities were calculated by integrating the fitted function in an interval of ±5° around the most probable angles.

From Fig. 6, it becomes visible, that the probabilities for the encapsulated complex are higher than those for the free complex. In other words, for a given simulation temperature the deviation of the observed angles from the most probable ones is for the encapsulated complex smaller than that of the free complex. The differing values between the left and right hand side of the encapsulated complex can be attributed to interactions with the zeolite framework and are larger for the large amplitude swinging vibration of the phenyl-rings.

By reducing the simulation temperature, the probabilities of the dihedral angles and the swing angles of

Table 1
Most probable dihedral and swinging angles of the Co-salen-complex inside and outside the zeolite matrix at different simulation temperatures

| T (K)	Homogeneous complex				Encapsulated complex			
	Swing angle		Dihedral angle		Swing angle		Dihedral angle	
	Left	Right	Left	Right	Left	Right	Left	Right
240	24.45 (14)	−25.97 (15)	11.19 (16)	11.00 (26)	–	–	–	–
250	27.83 (17)	−28.08 (15)	13.23 (13)	12.93 (12)	–	–	–	–
260	28.35 (16)	−29.20 (17)	13.22 (14)	13.60 (14)	22.24 (24)	−14.35 (44)	9.51 (17)	3.79 (16)
270	24.48 (17)	−26.68 (19)	12.45 (13)	12.43 (13)	20.86 (25)	−17.36 (28)	8.95 (13)	3.704 (67)
280	24.48 (26)	−25.33 (24)	12.88 (14)	12.24 (24)	29.21 (38)	−15.99 (33)	14.96 (20)	9.38 (30)
290	25.12 (15)	−25.94 (14)	12.07 (15)	12.31 (16)	16.40 (47)	−21.54 (43)	−4.99 (12)	7.79 (16)
300	25.08 (23)	−25.22 (21)	11.75 (25)	12.42 (23)	20.97 (27)	−17.89 (42)	8.24 (12)	4.82 (16)
310	22.97 (40)	−29.70 (98)	11.04 (21)	11.30 (34)	21.31 (48)	−16.75 (30)	8.338 (74)	2.95 (13)

The errors of the last digits are given in parenthesis.
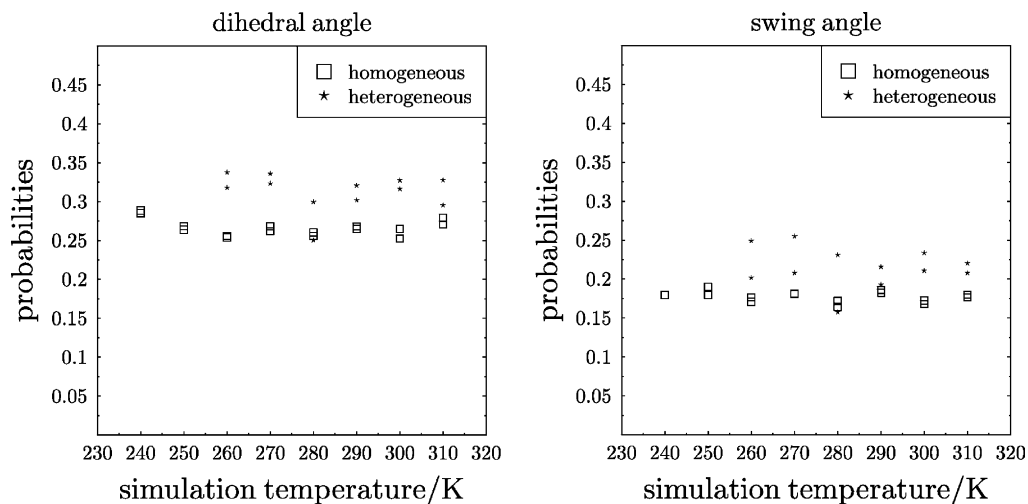
Fig. 6. Probabilities to find the simulated dihedral angles (left) and swing angles (right) inside an interval of $\pm 5°$ around the most probable angle.

the free and encapsulated complex as seen in Fig. 6 are approaching a common value.

The analysis of the cyclohexyl backbone results in a unspecific vibration of the carbon atoms above and below the $N-CO-N_1$ plane. The probability distribution is symmetric with respect to the $N-CO-N_1$ plane, and the FWHH of the probability distribution increase with increasing distance from the metal atom.

3. Conclusion

Molecular dynamics simulations of an occluded and a free Co-salen-complex were performed at several simulation temperatures. With respect to the different published epoxidation mechanisms observables were defined and the vibrations of the two salen-complexes were analyzed. It could be seen, that the occluded complex is distorted in a way, that a path for the approaching substrate is blocked. Furthermore, at a given temperature, the encapsulated complex changes its conformation less than the free complex, i.e. the complex inside the zeolite is more confined to a certain structure than outside the zeolite. The movement of the cyclohexyl-group is compared to the movements of the phenyl-groups small.

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