Novel zeolitic hosts for “ship-in-a-bottle” catalysts

Carmen Heinrichs and Wolfgang F. Hölderich [*]

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

Received 1 July 1998; accepted 17 February 1999

Modified faujasites have been employed in order to incorporate sterically demanding organometallic complexes such as the Jacobsen catalyst in zeolites X and Y. The new heterogeneous catalysts have been tested in the diastereoselective epoxidation of (R)-$(+)$-limonene in the liquid phase in an autoclave at elevated pressure using O_2 as the oxidant as well as in a glass reactor at ambient pressure using NaOCl as the oxidizing agent. In both catalytic systems conversions of 100% could be achieved. Selectivities were up to 70% and de values up to 55% in the autoclave experiments whereas in the experiments at atmospheric pressure they remained below 10 and 30%, respectively.

Keywords: heterogeneous catalysis, zeolites, epoxidation, olefin

1. Introduction

Recent developments in the area of oxidation catalysis resulted in a growing interest in organometallic compounds encapsulated in zeolites. Thereby the zeolite-entrapped metal complex is free to move within the confined cavities of its crystalline host but prevented from leaching by restrictive pore openings. This can be achieved by the physical occlusion of metal complexes in zeolitic micro- or mesoporous space via the “ship-in-a-bottle” synthesis method. It can be assumed that “ship-in-a-bottle” catalysts provide many advantages in catalysis that cannot be achieved by homogeneous or conventional heterogeneous catalytic systems where the metal complex is attached to a solid surface by a covalent or ionic bond. Advantages of “ship-in-a-bottle” catalysts over homogeneous systems are, e.g., their enhanced thermal stability, their easy separation from the reaction mixture and, thus, their resulting recyclability and environmental inoffensiveness. Regarding conventional heterogeneous catalysts the main advantage of “ship-in-a-bottle” catalysts is the enhanced accessibility of the catalytical active metal complex due to its ability to move freely within the zeolite’s cavity. In addition, because of the nature of their immobilisation, i.e., the physical entrapment in zeolite pores, “ship-in-a-bottle” catalysts are unlikely to leach. Furthermore, it is likely that the crystalline host bestows size and shape selectivity to the catalyst as well as a stabilizing effect on the organometallic complex since multimolecular deactivation pathways such as formation of μ-oxo- or peroxo-bridged species will be rendered impossible [1].

The (salen)manganese-catalyzed oxidation of olefins is currently investigated by various groups, e.g., Jacobsen et al., Katsuki et al., Jacobs et al., and Corma et al. [2–5]. Various attempts have been made to enhance the performance of the system first introduced by Jacobsen in 1991 [6], e.g., exchange of the *tert*-butyl groups in *ortho* and *para* positions of the salicylidene moieties of the ligand [7] or substitution of NaOCl as oxidant [3,8,9]. Different approaches have been made to attempt the immobilization of the Jacobsen catalyst, e.g., its embedding in a polydimethylsiloxane membrane [4]. Its entrapment in zeolitic space, however, has presented a problem so far, with the average faujasite supercage (13 Å in diameter) being too small a cavity for such a spaceous complex so that only complexes of the less bulky bissalicylidene-1,2-cyclohexanediamine have been successfully occluded in faujasites [5,10].

We here present now a method of post-synthetic zeolite modification which allows us to generate mesopores surrounded by microporous space. In these mesopores we have synthesized the bulky Jacobsen catalyst with the ligand (R,R')-(N,N')-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine and we have therefore successfully accomplished for the first time the immobilization of the Jacobsen catalyst in a faujasite type zeolite.

Due to the importance of oxygenated monoterpenes as flavour and perfume compounds we investigated our “ship-in-a-bottle” catalyst’s performance in the oxidation of (R)-$(+)$-limonene. We are the first to describe the heterogeneously catalyzed diastereoselective epoxidation of (R)-$(+)$-limonene, in which our catalyst showed promising results regarding conversion, selectivity and chiral induction.

2. Experimental

2.1. Catalyst preparation

In a typical dealumination procedure, 5–10 g of zeolite X or Y (sodium form) in deep bed were dried for 12 h

---

[*] To whom correspondence should be addressed.

at 723 K under a steady flow of dry nitrogen (3 l/h) in a horizontal tubular quartz reactor with an internal diameter of 3 cm (heating rate: 5 K/min). A nitrogen stream was saturated with silicon tetrachloride at room temperature and passed through the zeolite sample at 523 K. After the $SiCl_4$ treatment was stopped nitrogen was still passed through the reactor in order to remove residual silicon tetrachloride while the sample was allowed to cool to room temperature. The material was ion-exchanged three times with ammonium acetate/ammonium chloride solution (NH_4OAc: 10 mol/l; NH_4Cl: 2 mol/l) at 353 K for 24 h for the removal of sodium. After washing and drying the zeolite was steamed for 3 h at 873 K, then once again ion-exchanged with 2 M ammonium chloride solution and afterwards steamed at 1123 K for another 3 h. Partial removal of the extra-framework aluminium species by treatment with aqueous hydrochloric acid at pH 2.7 and room temperature was followed by an ion exchange with manganese acetate tetrahydrate for the introduction of manganese(II) ions. The ion-exchanged zeolite was then dried under vacuum at 823 K (heating rate: 1 K/min) and cooled under inert atmosphere before synthesis of the salen ligands in the mesopores. The ligand synthesis was conducted under an inert atmosphere and started with the addition of an amount of $(1R,2R)$-$(-)$-1,2-diaminocyclohexane in dichloromethane equimolar to the manganese loading. After stirring for several hours the appropiate amount of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde in dichloromethane was added to the slurry and stirring was continued. The mixture was transferred into an extraction thimble and was soxhlet-extracted with dichloromethane until the solvent remained colourless.

2.2. Characterization

The wet chemical analysis was done on an inductive coupled plasma atomic emission spectroscope (ICP-AES) Spectroflame D (Spectro). Typically, 30 mg sample was dissolved in 500 μl 40% HF solution, 4 ml 1 : 4 H_2SO_4 solution and 45 ml H_2O.

Infrared Fourier transform spectroscopy (FT-IR) was performed at room temperature on a Nicolet spectrometer 510 P using standard KBr techniques.

For thermogravimetric analyses a Netzsch 209/2/E equipped with a STA 409 controller was used. The heating rate was 5 °C/min, using Al_2O_3 crucibles; α-Al_2O_3 was used as the reference material.

Nitrogen adsorption/desorption isotherms were determined with a Micromeritics ASAP 2010 at 77 K.

UV/VIS spectra were collected on a Lambda 7 (Perkin–Elmer). If necessary the samples were diluted with $BaSO_4$ which was also used as the standard. The recording speed was 60.0 nm/min, the data interval 1.0 nm and the slit width 4.0 nm.

GC analysis was performed on a HP 6890 series gas chromatograph (Hewlett–Packard) using a 60 m 1701 (CP-Sil 19) column and on a Siemens RGC 202 gas chromatograph with a Chromjet Integrator (Spectra-Physics) using a 25 m Lipodex E column.

Details of the investigation are described in section 3.

2.3. Catalytic testing

The oxidation of (R)-$(+)$-limonene had been performed in a 75 ml stainless steel autoclave with oxygen pressures from 10 to 40 bar as well as in a glass reactor at atmospheric pressure.

In a typical autoclave run 30 ml fluorobenzene, 1.2 ml (R)-$(+)$-limonene (7.42 mmol), 0.3 ml N-methylimidazole (3.77 mmol) and 2.49 ml pivalaldehyde (22.9 mmol) were, quite similar to Mukaiyama et al. [9], added to 100 mg of catalyst at room temperature. After sealing the autoclave 30–40 bar of oxygen were added and the reaction mixture was stirred vigorously for 24 h.

In a typical run at atmospheric pressure, 1.2 ml (R)-$(+)$-limonene (7.42 mmol) in 15 ml dichloromethane were added to 100 mg of catalyst at 278 K. 15 ml commercially available NaOCl solution (household bleach) [5,6,16] were added to the vigorously stirred reaction mixture and stirring was continued for 10 days.

3. Results and discussion

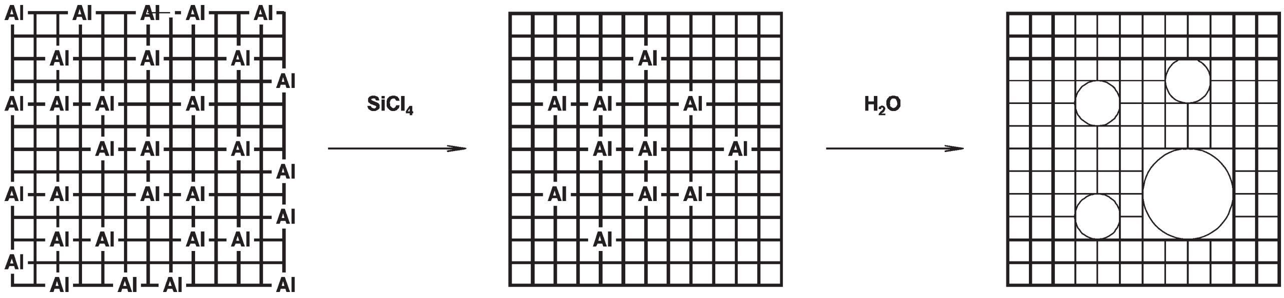
The results of the dealumination procedure are summarized in table 1. The SiO_2/Al_2O_3 ratios of the dealuminated zeolites have been determined by IR spectroscopy using the external symmetric stretch assigned to an Al–O vibration [11].

During treatment with silicon tetrachloride, a dealumination method first reported by Beyer et al. [12], the faujasite's framework aluminium is isomorphously replaced by silicon. Upon removal from the reactor the samples are of a slightly yellow colour indicating the presence of $NaAlCl_4$. Although the reaction time ranged from 40 to 150 min the small range of the SiO_2/Al_2O_3 ratios (3.9–5.2 for zeolite X and 12.7–15.3 for zeolite Y) suggests that for this kind of treatment a maximum degree of dealumination has been reached. Therefore, it can be assumed that upon $SiCl_4$ treatment of a zeolite crystal $NaAlCl_4$ will precipitate in the outer layer of the zeolite pores and terminate the progression of the dealumination reaction [13].

During the successive ion exchange these chloroaluminium complexes are extracted and the zeolite is converted into the ammonium form. The second dealumination step results in SiO_2/Al_2O_3 ratios of 6.3–9.0 for zeolite X and 27.3–32.6 for zeolite Y, respectively. Conducting the first steaming at temperatures above 873 K causes destruction of the zeolite structure. Upon the second steaming at 1123 K a high degree of dealumination is achieved with a SiO_2/Al_2O_3 ranging from 125.1 to 188.7 for both zeolites X and Y. Using the described dealumination procedure over all steps highly dealuminated faujasites are obtained regardless of the parent material. Final treatment with hy-

Table 1
Results of the dealumination procedure.

Zeolite	SiO_2/Al_2O_3			
	Parent material	After $SiCl_4$ treatment	After 1st steaming	After 2nd steaming
MnX-22	3.0	3.9	6.6	125.1
MnX-24	3.0	4.7	6.3	188.7
MnX-26	3.0	5.2	9.0	188.7
MnY-38	6.3	15.3	29.8	188.7
MnY-40	6.3	12.7	27.3	125.1
MnY-42	6.3	15.3	32.6	188.7



Scheme 1. The steps of the dealumination procedure.

Table 2
Characterization of the zeolitic hosts.

Zeolite	SiO_2/Al_2O_3	Nitrogen adsorption		
		BET surface area (m^2/g)	Micropore volume (cm^3/g)	BJH volume (cm^3/g)
Parent X	3.0	659.8	0.300	–
Parent Y	6.3	721.6	0.328	–
MnX-22	125.1	346.2	0.132	0.183
MnX-24	188.7	355.7	0.123	0.195
MnX-26	188.7	361.1	0.124	0.173
MnY-38	188.7	615.5	0.265	0.060
MnY-40	125.1	599.5	0.258	0.070
MnY-42	188.7	621.2	0.268	0.079

drochloric acid partially removes the extra-framework aluminium and results in the crystalline hosts for organometallic complexes. Complete removal of the extra-framework aluminium species renders the zeolite less stable under alkaline and hydrothermal conditions and leads to a collapse of the zeolite structure [14].

In table 2 data of nitrogen adsorption measurements are shown.

Upon dealumination the parent X has lost up to 48% of its BET surface area (MnX-22) and up to 41% of its micropore volume (MnX-24) without, due to XRD investigations, destruction of the zeolite structure. The total volume of the generated mesopores amounts up to 0.195 cm^3/g in zeolite X. The parent Y has obtained considerably less mesopore volume (0.060–0.079 cm^3/g) after the dealumination procedure but has also lost only about 17% of its BET surface area and 21% of its microporous volume (both MnY-40). The dealumination products' difference in composition is due to the different aluminium contents of the parent materials. Therefore, the aluminium-richer X zeolites obtain a larger mesopore volume and experience a greater loss of BET surface area and micropore volume than the aluminium-poorer Y zeolites.

Table 3
Catalyst characterization.

Catalyst	Parent zeolite	Si/Mn ratio	Ligand[a]	Ligand loading (wt%)
1	NaMnY	16	2	8.6
2	MnX-24	324	1	2.1
3	MnX-26	427	1	3.3
4	MnY-38	305	1	2.2
5	MnY-40	235	1	1.9
6	MnY-42	305	1	2.2
7	MnX-28	119	1	5.5
8	MnX-24	74	2	6.4

[a] Ligand 1: (R,R')-(N,N')-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine. Ligand 2: (R,R')-(N,N')-bissalicylidene-1,2-cyclohexanediamine.

Data of the catalyst characterization are shown in table 3. The determination of the Si/Mn ratio is based on ICP-AES analysis. Ligand loadings were determined using thermogravimetry. Due to their slow decomposition during a broad range of temperature, starting at 523 K and ending at about 823 K, it is not possible to acquire an exact temperature of decomposition for the "ship-in-a-bottle" catalysts. According to our thermogravimetric investigations the free salen ligands as well as the homogeneous Jacobsen catalyst decompose in two steps, the decomposition temperatures being 586 and 674 K for the ligand (R,R')-(N,N')-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, 571 and 756 K for the ligand (R,R')-(N,N')-bissalicylidene-1,2-cyclohexanediamine, and 605 and 694 K for $[N,N'$-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato (2-)]manganese(III) chloride, respectively.

According to its higher amount of sodium that could be exchanged with manganese and the greater number of supercages in its intact microporous structure the NaMnY not subjected to the dealumination procedure has both the highest Mn content and the highest ligand loading. As predicted by molecular modelling, only the less spaceous ligand (R,R')-(N,N')-bissalicylidene-1,2-cyclohexanediamine has been successfully incorporated into that NaMnY, the ligand (R,R')-(N,N')-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine with its four *tert*-butyl groups has proved to be far too bulky for occlusion. Due to the generated mesopore volume the dealuminated samples are not only able to host the ligand (R,R')-(N,N')-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, as shown by FTIR and UV/VIS spectroscopy they also contain a slight excess of ligand regarding the manganese content.

In figure 1 the FTIR spectra of the Jacobsen catalyst (A), the Jacobsen ligand (B) and our catalyst 2 (C) are compared. The spectra of catalysts 1 and 3–8 are similar to the one of catalyst 2 (C). While the spectra A and B have been done using standard KBr technique, the "ship-in-a-bottle" catalyst (C) has been prepared as a self-supported wafer. The bands at wavenumbers 1466, 1434, 1399 and 1365 cm^{-1}, appearing in all three of our spectra, can be assigned to the salen ligand whereas the characteristic band of the complex at 1535 cm^{-1} can only be found in spectra A and C. These results are in accordance to data published earlier by Corma et al. [5] for the zeolite-occluded (R,R)-(N,N')-bissalicylidene-1,2-cyclohexanediaminato(2-)manganese(III) complex, i.e., the Jacobsen catalyst without its four tertiary butyl groups. That can be considered as proof to the presence of the Jacobsen complex, $[(R,R)$-(N,N')-bis(3,5-di-*tert*-butylsalicylidene-1,2-cyclohexanediaminato(2-)manganese(III)$^+$, in our "ship-in-a-bottle" catalyst.

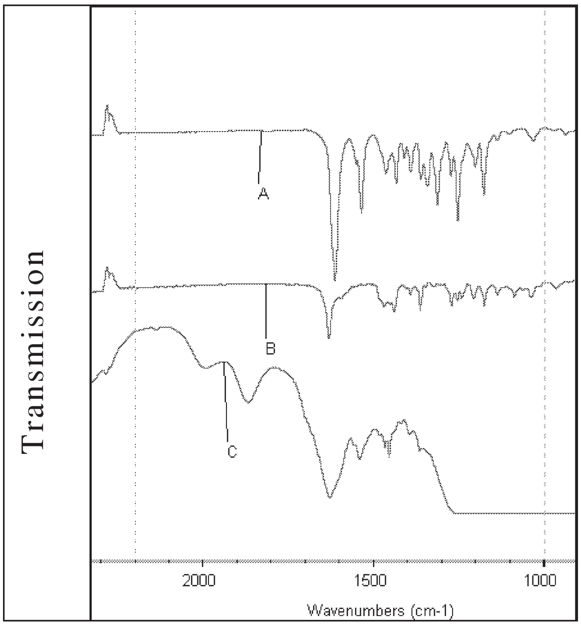


Figure 1. FTIR spectra of the Jacobsen catalyst (A), the Jacobsen ligand (B) and our heterogeneous catalyst (C). Note that the 1535 cm^{-1} band assigned to the complex is present in the spectrum of the heterogeneous catalyst.

Figure 2 shows UV-VIS investigations that have been done on the Jacobsen catalyst, the Jacobsen ligand and the "ship-in-a-bottle" catalyst 2. The spectra of catalysts 1 and 3–8 are similar to the one of catalyst 2. The homogeneous Jacobsen catalyst proved to be unsuitable for comparison because it absorbs in the whole spectral range. The shoulder at 430 nm as well as the bathochromic shift of the absorption band of the Jacobsen ligand hint at the presence of aggregated molecules [15]. The adsorption bands of the salen ligand as well as a slighter version of the above mentioned shoulder can also be found in the spectrum of catalyst 2. This indicates, in accordance to results published earlier by Corma et al. [5], the presence of free Jacobsen ligand in the "ship-in-a-bottle" catalyst.

In table 4 the results of the experiments at ambient pressure are summarized. All experiments have been repeated twice.

All experiments at atmospheric pressure have a poor epoxide selectivity and modest de values in common. Also low selectivity but higher de have been found for the two runs with the homogeneous Jacobsen catalyst. The broad product spectrum contains besides the desired limonene epoxide a mixture of aldehydes and ketones obtained by the rearrangement of epoxides, olefins and further oxidized products. Catalytic runs were conducted with commercially available household bleach which had been according to Jacobsen et al. [16] diluted 1 : 2 with an aqueous Na_2HPO_4 solution (7 g/l) for experiments 4-P and Jacobsen catalyst-P. As can be seen by the comparison of experiments 4-P and 4, and of Jacobsen catalyst-P and Jacobsen catalyst, respectively, the Na_2HPO_4 additive did not cause any difference in the outcome of the catalytical tests. The experiments confirmed earlier results found by Corma et al. [5] with the the Mn-(N,N')-bissalicylidene-1,2-cyclohexanediamine complex entrapped in zeolite Y.

The results of the autoclave experiments are summarized in table 5. All experiments have been conducted twice.

In the autoclave runs at all tested "ship-in-a-bottle" catalysts achieved high conversion regardless of the zeolitic host, the Si/Mn ratios and the amount or nature of

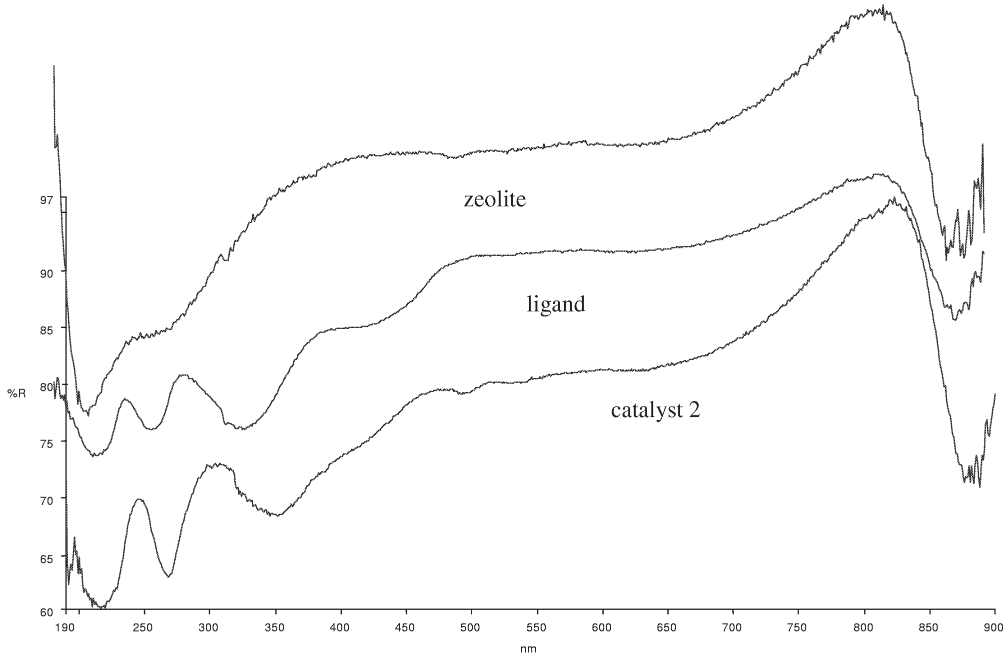


Figure 2. UV-VIS spectra of the zeolitic host, the Jacobsen ligand and our heterogeneous catalyst.

Table 4
Conversion, selectivities and de of the experiments at ambient pressure.

Catalyst	Conversion (%)	Selectivity (%)	de[a] (%)
1	62	2	26
4-P	100	5	21
4	100	9	20
Jacobsen catalyst	100	4	81
Jacobsen catalyst-P	95	7	71

[a] Excess of the *cis*-epoxide.

Table 5
Conversion, selectivities and de of the autoclave experiments.

Catalyst	Conversion (%)	Selectivity (%)	de[a] (%)
1	100	38	55
6	100	41	48
5	100	39	46
7	100	39	32
3	100	32	43
8	100	45	42
8[b]	95	66	41
8[c]	93	70	40

[a] Excess of the *cis*-epoxide.
[b] Reaction conducted under O_2 pressure of 20 bar.
[c] Reaction conducted under O_2 pressure of 10 bar.

the salen ligand. Epoxide selectivities ranged from 32 to 70% and de values were 32–55%, respectively. Catalyst 1, consisting of (R,R')-(N,N')-bissalicylidene-1,2-cyclohexanediamine hosted in the NaMnY which had not been subjected to the dealumination procedure, achieved the highest de. The highest selectivity at 30 bar oxygen pressure was obtained by catalyst 8, a MnX which hosts the same salen ligand. Catalytic runs with catalyst 8 at lower pressures showed that with decreasing oxygen pressure the epoxide selectivity could be increased up to 70% (10 bar O_2 pressure) without a significant decrease in conversion. According to GC-MS analysis the by-products of the reaction consisted of the twice epoxidized limonene and some rearrangement products.

In order to investigate if our zeolite contributes to the product spectrum other than to serve as a host to the active compound, we conducted several catalytic experiments with the unloaded modified faujasite as well as with the manganese-exchanged material prior to ligand synthesis. According to GC analysis no reaction took place. To establish the lack of leaching of the complex, we performed chemical analysis of the liquid after reaction. No Mn ions could be detected. We further investigated the aspect of leaching by separating the catalyst from the reaction mixture by filtration before total consumption of the olefin had been achieved. A sample was taken and analyzed by GC. The remaining, now catalyst-free reaction mixture was stirred additionally for several hours under oxygen atmosphere before another sample was taken and subjected to GC analysis. Comparison of the GC results of these two samples showed that after separation of the “ship-in-a-bottle” catalyst no further reaction had occurred.

4. Conclusion

Zeolites X and Y have been highly dealuminated by a succession of different dealumination methods, i.e., dealumination by treatment with $SiCl_4$ and dealumination by steaming, generating mesopores which are surrounded by microporous space. This could be proved by the occlusion of the Jacobsen catalyst and by means of nitrogen adsorption and FTIR-spectroscopy.

The Jacobsen catalyst [N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato(2-)]manganese(III) chloride has been entrapped in these mesopores of such highly dealuminated faujasites. The Mn-(R,R')-(N,N')-bissalicylidene-1,2-cyclohexanediamine complex has been occluded in faujasite supercages as well as in the modified micro-/mesoporous faujasites as "ship-in-a-bottle" catalysts. That could be demonstrated by means of thermogravimetry, FTIR and UV/VIS spectroscopy and soxhlet extraction. These "ship-in-a-bottle" catalysts have been investigated in the diastereoselective epoxidation of limonene. In the autoclave experiments at room temperature and with molecular oxygen at elevated pressure as the oxidizing agent better selectivities and chiral induction were found than in the experiments at 278 K using NaOCl as the oxidant, regardless of the "ship-in-a-bottle" catalyst's nature.

Acknowledgement

We wish to thank the Deutsche Forschungsgemeinschaft (DFG), Sonderforschungsbereich 380, for financial support of this work.

References

[1] K.J. Balkus, Jr., A.K. Khanmamedova, K.M. Dixon and F. Bedioui, Appl. Catal. A 143 (1996) 159.

[2] E.N. Jacobsen, in: *Catalytic Asymmetric Synthesis*, ed. I. Ojima (VCH, New York, 1993) p. 159.

[3] T. Katsuki, J. Mol. Catal. A 113 (1996) 87.

[4] I.F.J. Vankelecom, D. Tas, R.F. Parton, V. Van de Vyver and P.A. Jacobs, Angew. Chem. 108 (1996) 1445.

[5] M.J. Sabater, A. Corma, A. Domenech, V. Fornés and H. García, J. Chem. Soc. Chem. Commun. (1997) 1285.

[6] W. Zhang and E.N. Jacobsen, J. Org. Chem. 56 (1991) 2296.

[7] A. Robert, A. Tsapara and B. Meunier, J. Mol. Catal. 85 (1993) 13.

[8] W. Adam, J. Jekö, A. Lévai, C. Nemes, T. Patonay and P. Sebök, Tetrahedron Lett. 36 (1995) 21, 3669.

[9] T. Yamada, K. Imagawa, T. Nagata and T. Mukaiyama, Chem. Lett. (1992) 2231.

[10] W. Kahlen, H.H. Wagner and W.F. Hölderich, Catal. Lett. 54 (1998) 85.

[11] J.R. Sohn, S.J. DeCanio and J.H. Lunsford, Zeolites 6 (1986) 225.

[12] H.K. Beyer and I. Belenykaja, in: *Stud. Surf. Sci. Catal.*, Vol. 5, eds. B. Imelik et al. (Elsevier, Amsterdam, 1980) p. 203.

[13] P.J. Grobet, P.A. Jacobs and H.K. Beyer, Zeolites 6 (1986) 47.

[14] W. Lutz, E. Löffler and B. Zibrowius, in: *Stud. Surf. Sci. Catal.*, Vol. 97, eds. L. Bonneviot and S. Kaliaguine (Elsevier, Amsterdam, 1995) p. 327.

[15] N. Röhrlich, E. Löffler, B. Zibrowius, L. Chassot and W.F. Hölderich, J. Chem. Soc. Faraday Trans. 94 (1998) 609.

[16] N.H. Lee, A.R. Muci and E.N. Jacobsen, Tetrahedron Lett. 32 (1991) 5055.