Oxidation of α-methylstyrene on an MCM-22 encapsulated \((R, R)^{-}\)-\(N, N'^{-}\)bis(3,5-di-\text{tert-}\)butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) catalyst

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Abstract: \((R, R)^{-}\)-\(N, N'^{-}\)bis(3,5-di-\text{tert-}\)butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) was encapsulated into MCM-22 using the zeolite synthesis method. The encapsulated catalyst proved to be active in the oxidation of α-methylstyrene with NaOCl with higher specific activity than the homogeneous catalyst. At the same time, this encapsulated catalyst was completely inactive in the hydrolytic kinetic resolution of racemic styrene oxide. This observation is in a good correlation with the assumption of the cooperative bimetallic mechanism proposed by Annis and Jacobsen.

Keywords: Oxidation, α-methylstyrene, MCM-22, encapsulation, \((R, R)^{-}\)-\(N, N'^{-}\)bis(3,5-di-\text{tert-}\)butylsalicylidene)-1,2-cyclohexanediaminocobalt(II)

1 Introduction

An increasing demand has developed recently towards the heterogenization of homogeneous complexes due to environmental and economic reasons. Expensive chiral catalysts have particularly attracted much interest. One of the most widely studied complexes is \((R, R)^{-}\)-\(N, N'^{-}\)bis(3,5-di-\text{tert-}\)butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride called Jacobsen’s catalyst [1-3]. Attempts have been made to immobilize this

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complex not only for the possibility to reuse but also to preclude deactivation [4,5]. These two characteristics are among the observed advantages of the heterogenized homogeneous complexes [6-8].

The most important problem with the encapsulation of the Jacobsen catalyst is the size of the complex. The Jacobsen complex is too large to fit into zeolites having FAU or EMT topologies. Consequently, not the complete catalyst but the partially substituted molecule was encapsulated. Not surprisingly, the catalytic results did not meet the expectations [4,5].

MCM-22 zeolite seems to be a good solution for the encapsulation of Jacobsen’s catalyst, because it has a very large supercage (7.1x18.2 Å in diameter) and the synthesis of this zeolite proceeds through a layered precursor [9]. At this stage of the synthesis the catalyst can be intercalated between the layers. The intact Jacobsen’s catalyst encapsulated in this way was an active and selective catalyst for the epoxidation of α-methylstyrene. The heterogenized catalyst exhibited both higher activity and higher enantioselectivity than the homogeneous counterpart [10]. Although the possibility for recycling was not studied, the heterogenized catalyst had all the expected advantages [11,12].

The cobalt analog of the Jacobsen complex was used to study the hydrolytic kinetic resolution of terminal epoxides [13,14]. This method is a recently developed way to produce chiral products. A mechanism was established on a heterogenized version of this catalyst describing a cooperative bimetallic way to proceed [15,16].

In this paper we want to report our effort for the encapsulation of the Co analogue of the Jacobsen catalyst into MCM-22 and the application of the heterogenized catalyst in the oxidation of α-methylstyrene and in the hydrolytic kinetic resolution of racemic styrene oxide.

2 Experimental

2.1 Materials

α-Methylstyrene, styrene oxide, acetonitrile, tert-butyl methyl ketone, sodium hydroxide, hexamethylenimine and \((R,R)-(\cdot,\cdot)-N,N\'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II)\) (I) (Fig. 1) were purchased from Aldrich and used as received.

2.2 Encapsulation of the complex

The MCM-22 synthesis was based on the published procedure using hexamethylenimine as template [9,17]. 0.92 g sodium aluminate and 0.65 g sodium hydroxide was dissolved in 124 ml distilled water. 7.5 g hexamethylenimine and 9.13 g silica gel were added to this solution. This mixture was heated at 150 °C for 7 days with rotation. After cooling to room temperature, the layered MCM-22 precursor was stirred overnight with an ethanolic solution of complex I. After filtration and drying, the precursor was heated at 280 °C for 16 h. The product material was washed with ethanol (stirring at room temperature for
Scheme 1 The structure of the \((R,R)-(\text{--})-N,N^\prime\text{-bis(3,5-di-tert-buty}l\text{salicylidene)-1,2-cyclohexanediaminocobalt(II) complex (I).\rangle\)

5 h) to remove organic compounds adsorbed on the outer surface.

2.3 Characterization of the catalyst

XRD diffratograms were recorded on a Philips PW–1830 diffractometer. FT-IR spectra of the Co complex and the heterogenized sample were recorded on a Bio-Rad FTS-65 A spectrophotometer in KBr pellets. The loading of the metal complex of the immobilized sample was determined by ICP-AES (JOBLIN YVON 24 type instrument) after dissolving the sample in conc. HNO₃.

2.4 Oxidation reaction

10 mg of complex I (16.6 µmol) was dissolved in 6 ml acetonitrile and the mixture was cooled to 4 °C with ice water. 6 ml of NaOCl solution (8 mmol) mixed with 5 ml of 0.05 M of Na₂HPO₄ was cooled to 4 °C. The pH was adjusted to 10.3 by 1 M NaOH and this mixture was added to the acetonitrile solution. The reaction was started by adding 1 ml of α-methylstyrene (7.7 mmol) to the reaction mixture under N₂ at 4 °C under magnetic stirring. Samples taken every 3 h were analyzed by GC (HP1 capillary column, 150 °C). In the case of the encapsulated catalyst, 250 mg of catalyst containing 6 µmol of complex I was used, with other conditions unchanged.

2.5 Hydrolysis

To study the hydrolytic kinetic resolution of racemic styrene oxide, 150 mg of MCM-22 encapsulated catalyst (3.6 µmol) was added to the mixture of 50 µl tert-butyl methyl ketone, 50 µl racemic styrene oxide (0.4 mmol), and 5.5 µl water (0.3 mmol). The reaction mixture was stirred gently at room temperature for 3 h and analyzed by GC (Cyclodex B column).
3 Results and discussion

The encapsulated version of complex I was prepared by the zeolite synthesis method using MCM-22 as a host material. The MCM-22 structure was determined by X-ray powder diffraction (Fig. 1) and the encapsulated catalyst (MCM-22 containing complex I) was also characterized by XRD (Fig. 2). The FT-IR spectra of the neat complex and the immobilized catalyst are shown in Fig. 3.

Fig. 1 The XRD pattern of MCM-22 as synthesized.

Fig. 2 The XRD pattern of MCM-22 containing the complex after calcination.
A comparison of these spectra shows that the heterogenized sample contains the complex I. As seen in Fig. 3 the characteristic bands of the complex at 1630 cm\(^{-1}\) and 2900 cm\(^{-1}\) are also appearing in the spectrum of the heterogenized sample. The spectra, of course, are only a proof for the presence of the complex, but not for the encapsulation. The FT-IR spectrum gives some indication for the presence of a small amount of hexamethylenimine template in the encapsulated sample. MCM-22 consists of two independent pore systems. The first involves two-dimensional sinusoidal channels. These channels should be partially occupied by hexamethylenimine under the conditions of the study since this section of template is desorbed only above 400 °C. The second pore system involves supercages, where the complexes are located. Hexamethylenimine might also be located in these cages during the synthesis but begins to desorb above 231 °C. Additionally, hexamethylenimine is probably lost during the intercalation process. Therefore, no residual hexamethylenimine is expected to occupy any supercages after calcination at 280 °C.

The catalytic activities of the homogeneous complex I and its encapsulated version were evaluated in the oxidation of \(\alpha\)-methylstyrene by NaOCl (Scheme 2). The conversion, product distribution and reaction rate values measured using complex I as a homogeneous catalyst are summarized in Table 1.

![Scheme 2 Oxidation of \(\alpha\)-methylstyrene (1) by sodium hypochlorite.](image-url)
Table 1 Conversion, product distribution and specific activity values in the oxidation of α-methylstyrene with NaOCl solution using complex I as a homogeneous catalyst.

After 3 h 2-phenylpropanal (3) was the primary product of the oxidation reaction on the homogeneous complex I, but after 20 h the amount of 2-methyl-2-phenyloxirane (2) was comparable to that of the aldehyde. 2-Phenylpropane-1,2-diol (4) was a byproduct of the reaction. Complex I is a chiral molecule but, in contrast to the Mn analogue, the main product of the oxidation reaction is the racemic aldehyde. This complex, therefore, is an unsuitable catalyst for the enantioselective epoxidation of α-methylstyrene.

The encapsulated complex I was also used as oxidation catalyst in the same reaction using identical reaction conditions (Table 2).

Table 2 Conversion, product distribution and specific activity values in the oxidation of α-methylstyrene with NaOCl solution using complex I encapsulated in MCM-22.

As Table 2 shows, the encapsulated catalyst was also active in the oxidation of α-methylstyrene. The product distributions were similar, while the specific catalytic activity was higher in the case of the encapsulated catalyst. It is known that in some cases the activities of heterogenized systems are superior to those of the homogeneous catalysts [18]. The improved performance of the heterogenized system can sometimes be explained by the site isolation [19].

The obtained catalytic results, particularly the higher specific activity of the heterogenized system can prove that the encapsulation of complex I is successful and has led to an active catalyst for the oxidation of α-methylstyrene to 2-phenylpropanal. It means that α-methylstyrene molecules can migrate from the solution to the active sites in the supercages of the MCM-22 system and the product molecules can migrate back into the solution. In other words the encapsulated complex I proved to be an active oxidation catalyst under the conditions applied.
Balkus and coworkers [10] studied a similar system using a Mn(Salen) type complex and detected no leaching of the complex. This was proved by separating the catalyst after 4 h from the reaction mixture and by starting a new reaction. No further conversion was observed. We made a similar observation with the encapsulated Co(Salen) catalyst separated after 9 h indicating again the lack of any leaching.

Jacobsen and coworkers have published that chiral cobalt-based salen complexes were active catalysts for the hydrolytic kinetic resolution of terminal epoxides. The kinetic resolution of the racemic mixture of styrene oxide could afford the mixture of the highly valuable \((R)\)-styrene oxide and \((S)\)-1-phenylethane-1,2-diol in high yield with high enantiomeric excess [14].

Since our encapsulated catalyst is the Co analog of the Jacobsen catalyst, we have tried to use the complex I encapsulated in MCM-22 in the hydrolytic kinetic resolution of racemic styrene oxide. Our encapsulated catalyst, however, was completely inactive in the reaction studied, in spite of the fact that it was an active catalyst in the oxidation of \(\alpha\)-methylstyrene.

Mechanistic studies made by Jacobsen and coworkers indicated, that the epoxide ring-opening reactions proceeded through a mechanism involving cooperative interaction between catalyst units [15]. Later Annis and Jacobsen reported the synthesis of polystyrene- and silica-bound chiral Co(Salen) complexes and their application in the kinetic resolution of terminal epoxides [16]. The effects on reactivity of varying catalyst loadings have provided information on the mechanism of epoxide ring-opening. Samples with high surface loadings were active catalysts in the hydrolytic kinetic resolution, while catalysts with low surface concentrations were completely inactive. The observed correlation between the degree of catalyst site-isolation and reaction rate was consistent with a cooperative bimetallic mechanism in the hydrolytic kinetic resolution of terminal epoxides.

Thus the observed complete inactivity of the complex I encapsulated in MCM-22 in the hydrolytic kinetic resolution is a good evidence for the presence of separated complex molecules in the supercages that is for the encapsulation of complex I inside the MCM-22.

4 Conclusions

(1) \((R,R)\)-\((-)\)-\(N,N'\)-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) complex was encapsulated into MCM-22.

(2) The catalyst proved to be active for the oxidation of \(\alpha\)-methylstyrene to 2-phenylpropanal with NaOCl and the specific activity of this catalyst was found to be higher than that of the homogeneous complex. However, the encapsulated catalyst is unsuitable for the enantioselective epoxidation of \(\alpha\)-methylstyrene since it affords the racemic aldehyde.

(3) The encapsulated catalyst was completely inactive in the hydrolytic kinetic resolution of racemic styrene oxide. This observation is consistent with the existence of the cooperative bimetallic mechanism proposed by Annis and Jacobsen and a
good evidence for the presence of separated encapsulated complex molecules in the supercages.

References

[1] D.E. De Vos, I.F.J. Vankelecom and P.A. Jacobs: Chiral Catalyst Immobilization and Recycling, Wiley-VCH, Weinheim, 2000.

[2] D.E. De Vos, M. Dams, B.F. Sels and P.A. Jacobs: “Ordered Mesoporous and Microporous Molecular Sieves Functionalized with Transition Metal Complexes as Catalysts for Selective Organic Transformations”, Chem. Rev., Vol. 102, (2002), pp. 3615–3640.

[3] C. Bianchini and P. Barbaro: “Recent aspects of asymmetric catalysis by immobilized chiral metal catalysts”, Topics Catal., Vol. 19, (2002), pp. 17–32.

[4] M.J. Sabater, A. Corma, A. Domenech, V. Fornes and H. Garcia: “Chiral salen manganese complex encapsulated within zeolite Y: a heterogeneous enantioselective catalyst for the epoxidation of alkenes” J. Chem. Soc., Chem. Commun., (1997), pp. 1285–1286

[5] S.B. Ogunwumi and T. Bein: “Intrazeolite assembly of a chiral manganese salen epoxidation catalysts” J. Chem. Soc., Chem. Commun., (1997), pp. 901–902.

[6] C. Reyes, Y. Gao, Á. Zsigmond, P. Goel, N. Mahata, S. Tanielyan and R.L. Augustine: “Solvent Effects in the Use of Anchored Homogeneous Catalyst for Hydrogenation Reactions”, Chemistry Industry (Dekker), Vol. 89, (2002), pp. 627–632.

[7] R.L. Augustine, S.K. Tanielyan, N. Mahata, Y Gao, Á. Zsigmond and H. Yang: “Anchored homogeneous catalysts: The role of the heteropoly acid anchoring agent”, Appl. Catal. A-General, Vol. 256, (2003), pp. 69–76.

[8] Á. Zsigmond, K. Bogár and F. Notheisz: “Comparative study of “Ship-in-a-bottle” and Anchored Rh Complexes”, J. Catal., Vol. 213, (2003), pp. 103–108.

[9] M.E. Leonowicz, J.A. Lawton and M.K. Rubin: “MCM-22 – a molecular sieve with two independent multidimensional channel systems”, Science, Vol. 264, (1994), pp. 1910–1913.

[10] G. Gbery, Á. Zsigmond and K.J. Balkus, Jr.: “Enantioselective epoxidations catalyzed by zeolite MCM-22 encapsulated Jacobsen’s catalyst”, Catal. Lett., Vol 74, (2001), pp. 77–80.

[11] Á. Zsigmond, F. Notheisz, Z. Fráter and J.E. Bäckvall: “Selective oxidation of alcohols on zeolite encapsulated cobalt salophen catalysts”, Studies in Surface Science and Catalysis, Vol. 108, (1997), pp. 453–459.

[12] Á. Zsigmond, F. Notheisz, G. Csjernyik and J.E. Bäckvall: “Ruthenium-catalyzed aerobic oxidation of alcohols on zeolite-encapsulated cobalt salophen catalyst”, Top. Catal., Vol. 19, (2002), pp. 119–124.

[13] R.G Konsler, J. Kaarl and E.N. Jacobsen: “Cooperative asymmetric catalysis with dimeric salen complexes”, J. Am. Chem. Soc., Vol., 120, (1998), pp. 10780–10781.

[14] M. Tokunaga, J.F. Larrow, F. Kakiuchi and E.N. Jacobsen: “Asymmetric catalysis with water: Efficient kinetic resolution of terminal epoxides by means of catalytic hydrolysis”, Science, Vol. 277, (1997), pp. 936–938.
[15] K.B. Hansen, J.L. Leighton and E.N. Jacobsen: “On the mechanism of asymmetric nucleophilic ring-opening of epoxides catalyzed by (salen)Cr-III complexes”, *J. Am. Chem. Soc.*, Vol. 118, (1996), pp. 10924–10925.

[16] D.A. Annis and E.N. Jacobsen: “Polymer-supported chiral Co(salen) complexes: Synthetic applications and mechanistic investigations in the hydrolytic kinetic resolution of terminal epoxides”, *J. Am. Chem. Soc.*, Vol. 121, (1999), pp. 4147–4154.

[17] I. Guray, J. Warzywoda, N. Bac and A. Sacco, Jr.: “Synthesis of zeolite MCM-22 under rotating and static conditions”, *Microporous Mesoporous Mater.*, Vol. 31, (1999), pp. 241–251.

[18] F. Notheisz, Á. Zsigmond, Zs. Szegletes and J.E. Bäckvall: “Aerobic oxidations on metal macrocycles encapsulated in zeolites”, *Studies in Surface Science and Catalysis*, Vol. 94, (1995), pp. 728–735.

[19] Á. Zsigmond, F. Notheisz and J.E. Bäckvall: “Rate enhancement of oxidation reactions by the encapsulation of metal phthalocyanine complex”, *Catal. Lett.*, Vol. 65, (2000), pp. 135–139.