

Cyclohexene oxidation with an iron cyclam-type complex encapsulated in Y-zeolite

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Abstract

The synthesis and characterization of an iron cyclam-type complex within the cavities of a Y-zeolite is described. By comparing the performance of the heterogeneous system with the free complex in the oxidation of cyclohexene using iodosylbenzene as oxygen donor, a protection effect of the matrix over the active center was evidenced by a higher turnover and yield of products. It was possible to determine, by UV-VIS spectroscopy, that the free complex suffers molecular degradation after two hours of reaction whereas the heterogeneous catalyst remains unaltered and active after 24 hours of reaction. The main products found in the catalyzed reaction were 2-cyclohexen-1-ol, 2-cyclohexen-1-one, epoxy-cyclohexane and cyclohexanol.

Keywords: Cyclohexene oxidation; Encapsulated complexes; Cyclam; Zeolite Y

1. Introduction

Many homogeneous catalysts for selective oxidation show a tendency to autooxidation and deactivation by μ -dimerization through the formation of oxygen bridges [1]. In order to avoid these problems, to improve the separation of the catalyst from the reaction medium and to increase its active life, the catalyst may be intercalated in a layered compound, like a clay or may be encapsulated within the cavities of a porous solid as a zeolite which could give additional selectivity by molecular sieving effects [2–5].

In this paper, we report the catalytic action of iron coordinated to the macrocyclic ligand 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotet-

radeca-4,6,11,13-tetraene (FeTMC), shown in Fig. 1, and the same complex encapsulated in Y-zeolite (FeTMC-Y) in the oxidation of cyclohexene with iodosylbenzene as oxygen donor. Similar complexes have been used in order to obtain information concerning the nature of the oxygenating intermediates in homogeneous conditions [6,7] and to evaluate the catalytic potential of the zeolite encapsulated complexes [8].

2. Experimental

2.1. Materials

Reagent-grade chemicals were used throughout this work and were obtained from J.T. Baker (acetylacetone, ethylenediamine, *tert*-butyl alcohol, methylene dichloride, xylene and

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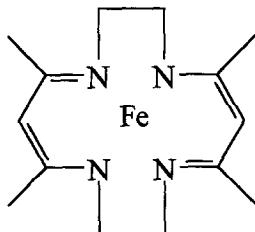


Fig. 1. Fe 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene (FeTMC).

HCl), Aldrich (ferrous sulphate heptahydrate, NaY zeolite lot No. 67812) and Merck (FeCl_2 , cyclohexene).

2.2. Synthesis of TMC

Acetylacetone (7 ml, 6.83 mmol) was slowly added to ethylenediamine (4 ml, 5.94 mmol), the precipitate was recovered by filtration, washed with ether and recrystallized in absolute ethanol.

2.3. Synthesis of FeTMC

The insertion of the metal in the macrocyclic ligand was carried out following the procedure reported by Holm and Truex [9]: FeCl_2 was added to a solution of the ligand TMC in *tert*-butyl alcohol at 60°C and stirred for 10 h. After that time the solvent was removed under reduced pressure and the product extracted and recrystallized in xylene. The process was done in nitrogen atmosphere.

2.4. Ionic exchange

Ionic exchange was done stirring NaY in an aqueous ferrous sulphate solution (0.025 M) during 48 hours, under nitrogen atmosphere. The ionic exchange degree was determined by atomic absorption.

2.5. Synthesis of FeTMC-Y

Working under dry nitrogen atmosphere, 0.40 g of the macrocyclic ligand TMC were dis-

solved in 80 ml of absolute *tert*-butyl alcohol. After the addition of 2 g of iron exchanged zeolite (NaFeY) the slurry was heated at 50–60°C and stirred for 18 hours to stimulate complex formation. In order to remove the excess of unreacted ligand from the surface of the zeolite, a Soxhlet extraction was carried out with *tert*-butyl alcohol during 72 hours.

2.6. Catalytic activity

The catalysts, FeTMC, FeTMC-Y and NaFeY (as control), were tested in the oxidation of cyclohexene using iodossylbenzene (PhIO) as oxygen donor in methylene dichloride. The reactions were carried out in batches with constant stirring at room temperature. The amounts used in a typical experiment are given in Table 1. Samples were taken at 20, 50, 70, 100, 130, 180 and 1440 minutes of reaction time. The products were identified by gas chromatography and mass spectrometry. The stability of the catalysts was determined by UV-VIS spectroscopy, taking spectra at different reaction times. The heterogeneous reaction was stopped after 24 hours, the catalyst was filtered off, dried and stirred with 4 ml of HCl for two hours to destroy the zeolitic structure and release the complex and other compounds physically trapped inside the matrix. FeTMC is soluble in HCl and the products were extracted with methylene dichloride.

2.7. Characterization

After completely destroying the zeolitic framework with hot and concentrated HCl, sodium, aluminum and iron were analyzed by atomic absorption and SiO_2 was determined by gravimetric analysis. The water percentage was

Table 1
Amounts used in a typical experiment

	Catalyst (g)	PhIO (g)	Cyclohexene (ml)
FeTMC	0.010	0.050	0.1
FeTMC-Y	0.5363	0.052	0.1
NaFeY	0.5112	0.050	0.1

measured by thermogravimetric analysis. TMC and FeTMC were characterized by IR, UV-VIS and NMR. FeTMC-Y was characterized by elemental analysis, IR, UV-VIS (destroying the zeolite with HCl), TGA, X-ray powder diffraction and XPS. The stability of the encapsulated catalyst was checked after the reaction by X-ray diffraction and UV-VIS and possible leaching of the complex was investigated by UV-VIS in the reaction solution after filtration of the catalyst.

UV-VIS electronic spectra were obtained using a Perkin-Elmer Lambda 4B spectrophotometer with a 1 cm path length cell in HCl and methylene dichloride.

IR spectra were carried out in a FTIR Perkin-Elmer model 1750 using thin KBr wafers.

NMR spectra (in CDCl_3) were taken in a Jeol EX-90.

Atomic absorption was measured in a Perkin-Elmer 372.

X-ray diffraction analysis was obtained in a Rigaku DMAX-III B, with Cu $K\alpha$ radiation and a graphite monochromator, scan speed 1 deg/min and scanning from 2 to 70 degrees.

Thermogravimetric analysis was carried out with a Cahn R-100 electrobalance adapted for thermogravimetric measurements with a heating rate of 5°C/min from room temperature to 600°C, in air.

XPS measurements were acquired at the Université Catholique de Louvain, Louvain-la-Neuve, Belgium, in a SSX-100 ESCA model 206 Surface Science Instrument (SSI). Binding energies were calculated with respect to the Si 2s peak set at 153.62 eV [10,11]; atomic ratios were calculated with the sensitivity factors proposed by the manufacturer; overlapping peaks were decomposed with the SSI software package on a Hewlett-Packard 9000 computer using a combination of Gaussian and Lorentzian shape without asymmetry. The Fe 2p peaks were decomposed into two main peaks each, imposing the following area constraints: the area of each $2p_{3/2}$ peak is twice the area of the corresponding $2p_{1/2}$.

GC/MS analyses: A Hewlett-Packard 5890 series II gas chromatograph with Hewlett-Packard 5972 selective mass detector and FID, with a capillary column DB5 60 m \times 0.25 mm \times 0.25 μm , was used for the identification and quantification of reactions products.

3. Results and discussion

3.1. Characterization

Chemical analysis: The chemical compositions of NaY, NaFeY and FeTMC-Y are given in Table 2. The ionic exchange was found to be of 10 Fe ions per unit cell with an average number of 1.25 Fe ions per supercage.

IR, UV-VIS, NMR: Table 3 shows the most important signals and their assignments. The IR and UV-VIS bands are in agreement with those reported by Holm and Truex [9]. After destroying the zeolitic framework with diluted HCl the characteristic UV-VIS signals of the complex were detected. During the reaction UV-VIS spectra of the homogeneous catalyst (Fig. 3) show notable changes indicating structural damage. These changes are not present in the heterogeneous system after 24 hours of reaction. After reaction the characteristic signal of FeTMC was not found in the electronic spectrum of the reaction solution. The zeolite holds the complex preventing leaching and protecting it against degradation.

TGA showed 23.3% water and gave 1.3% in weight of organic matter in the encapsulated system (1 molecule per unit cell), therefore one of every ten exchanged iron atoms form the coordination compound, this agrees with the presence of two iron peaks in XPS.

Table 2
Chemical composition of NaY, NaFeY and FeTMC-Y

	Si (%)	Al (%)	Na (%)	Fe (%)	Si/Al (%)
<i>Atomic ratios</i>					
NaY	22.2	8.97	7.28	–	2.39
NaFeY	20.38	7.48	3.47	2.10	2.66
FeTMC-Y	22.10	8.02	4.64	2.65	2.63

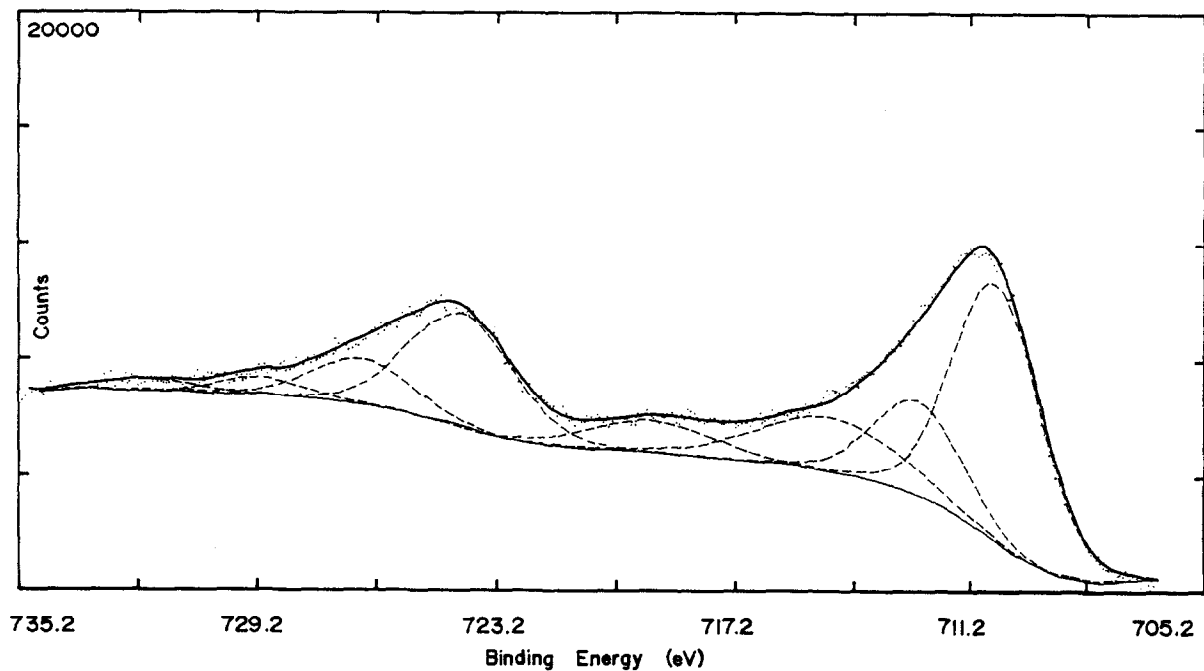
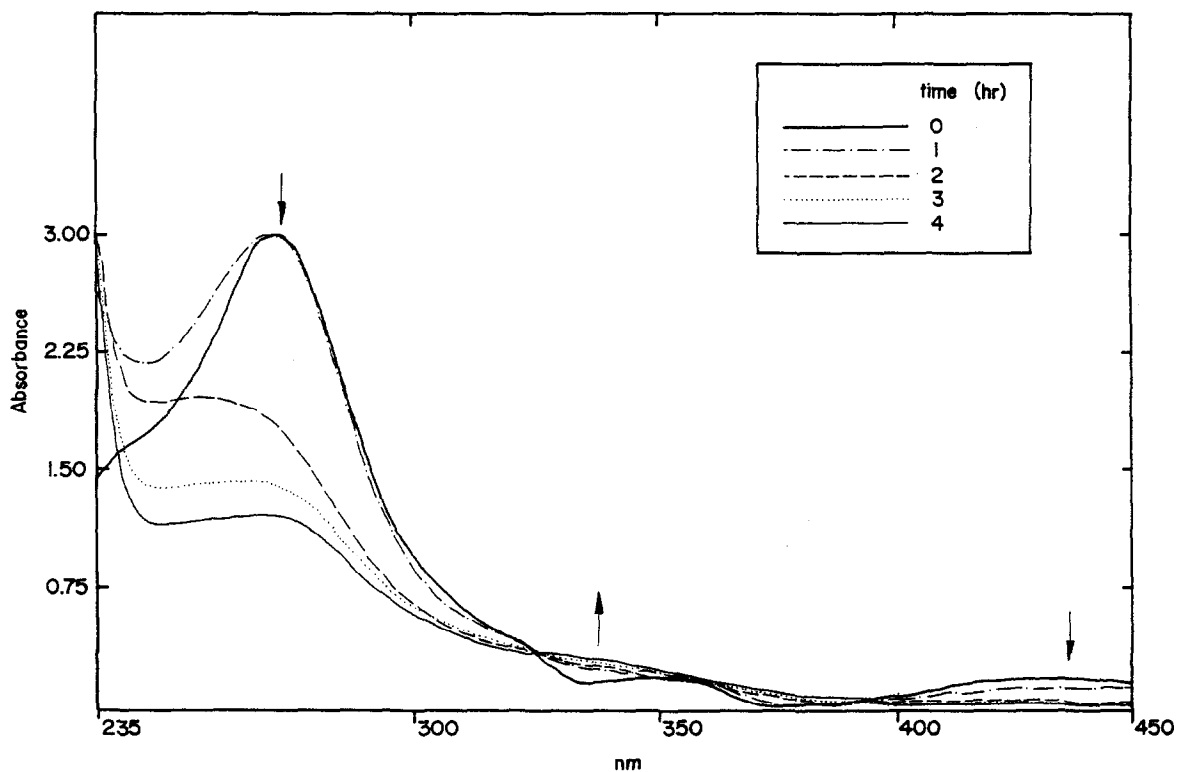
Fig. 2. XPS spectrum of Fe_{2p} in FeTMC-Y.

Fig. 3. Changes of the UV-VIS spectrum of FeTMC in the reaction medium.

Table 3
IR, electronic and NMR data for FeTMC

Spectrum	Signal	Assignment
IR	3195	N–H stretching
	1577, 1610	C=N and C=C stretching
	1385, 1434	CH ₂ , CH ₃ bendings
UV-VIS	270–280	Charge transfer
NMR	1.90	H ⁺ methylic
	3.40	H ⁺ methylenic
	4.95	H ⁺ methynic

XPS results are given in Tables 4 and 5 and Fig. 2. In FeTMC-Y, the two Fe 2p_{3/2} peaks with a separation over 2 eV indicate that iron is present in two different electronic environments as expected for the exchanged iron and the one bound to the nitrogens of the ligand. The very high C-to-N ratio (Table 4) shows a strong carbon contamination on the surface. The low N-to-Fe ratio on the surface (Table 4) indicates that only one in twelve iron atoms is bound to nitrogen ($N/Fe_{XPS} = 0.45$ vs. $N/Fe_{theor.} = 4$), this value is lower than the amount of coordinated iron (1 in 10) found via TGA. The fact that the complex concentration near the surface is lower than the one found in the bulk indicates that the complex is within the zeolite and not on its surface. Si-to-Al ratio shows surface enrichment of silicon as reported by Kaushik et al. [12].

3.2. Catalytic tests

Turnovers per day are given in Table 6. These values are similar or slightly higher than those obtained with porphyrins and salen occluded in zeolites [13,14] but yet far from the natural systems. The higher turnover obtained

Table 4
Atomic ratios

	FeTMC-Y (XPS)	FeTMC (calculated)
Si/Al	3.55	–
N/Fe	0.45	4.0
C/N	13.51	3.5

Table 5
Binding energies in FeTMC-Y in eV

Si 2s	153.6			
Al 1s	74.2			
Na 1s	1072.0			
O 1s	531.7			
C 1s	284.8	286.6	288.9	
N 1s	400.2	402.0		
Fe 2p ₃	710.5	712.4	714.7	719.1
Fe 2p ₁	723.9	726.4	728.9	731.7

with the heterogeneous system evidences the protective effect that the matrix performs over the coordination compound and in 24 hours its turnover is three times higher than that from the free complex.

Decrease of activity in both catalysts after 120 minutes of reaction is noticeable. Deactivation of the homogeneous catalyst is due to structural damage as evidenced by UV-VIS spectra; in the heterogeneous catalyst the apparent deactivation is not caused by destruction of the active center but by the clogging of the pores of the matrix due to the trapping of substrate and products of reaction within the zeolite, as also found by Herron [15]. These compounds were released, identified, quantified and added to the products previously found in the heterogeneous reaction solution at 1440 minutes. Fig. 4 shows the yields obtained with each catalytic system for the different products. As for product distribution, the reaction solutions of both the free and encapsulated complex gave 2-cyclohexen-1-ol > 2-cyclohexen-1-one > epoxide > cyclohexanol; while the products trapped within the zeolite showed epoxide > 2-cyclohexen-1-ol > 2-cyclohexen-1-one and only

Table 6
Turnover (moles of products^a/moles of catalysts) per day in the oxidation of cyclohexene at different reaction times

Time (min)	20	50	130	1440
FeTMC	60.96	24.48	11.28	2.16
FeTMC-Y	80.64	32.16	12.24	6.48 ^b
NaFeY	8.81	2.65	1.98	1.23

^a In solution.

^b Total (in solution plus trapped in zeolite).

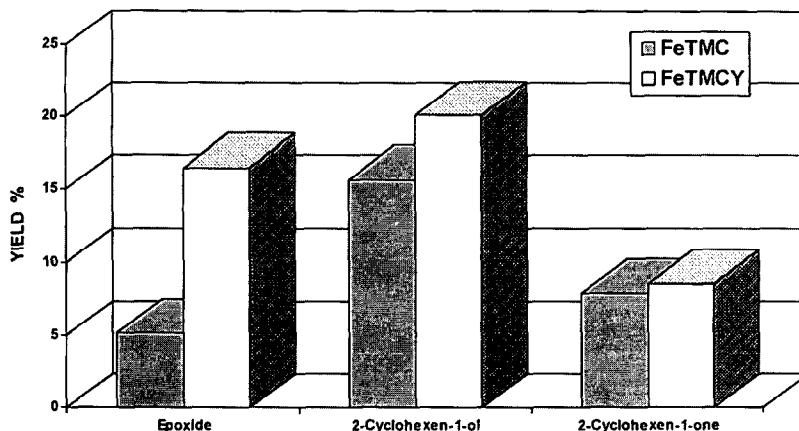


Fig. 4. Yields of oxidation products of cyclohexene, based on PhIO.

traces of cyclohexanol. The product distribution changed with time and was different for the free and encapsulated complex. Table 7 shows the percentage of each compound taking into account only the epoxide, 2-cyclohexen-1-ol, 2-cyclohexen-1-one and cyclohexanol. It seems that the zeolite not only protects the complex but also increase the epoxide yield. Cyclohexene conversion was 30% with the free complex and 40% for the encapsulated.

It has been claimed that it is possible to carry out oxidation of olefins with iodosylbenzene using Lewis acidic catalysts such as iron salts [16]. Control experiments gave oxidation products with iodosylbenzene in absence of the complex, as also found by Páez-Mozo et al. [2] and Gaigneaux et al. [17], however the low turnover obtained in control experiments with the iron

exchanged zeolite (Table 6, entry 3), indicates that the catalytic activity is mainly due to the complex.

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Table 7

Composition (%) of the reaction solution and trapped products at different reaction times

	20 min		1440 min		trapped
	FeTMC solution	FeTMC-Y solution	FeTMC solution	FeTMC-Y solution	
Epoxide	40.9	27.2	22.0	29.5	50.8
2-Cyclohexen-1-ol	33.3	28.9	48.3	35.1	32.1
2-Cyclohexen-1-one	18.5	43.9	19.7	24.0	16.7
Cyclohexanol	7.3	—	10.0	11.4	0.4

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