

Cationic metalloporphyrins and other macrocyclic compounds in zeolite matrix as catalysts for oxidation with dioxygen

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Abstract

Syntheses and catalytic activity of the cationic iron, manganese, cobalt porphyrins, cobalt salen and cobalt phthalocyanine in homogeneous reaction and these metallocomplexes entrapped inside zeolite NaX supercages have been studied in oxidation of cyclooctane with dioxygen (as air) to cyclooctanone and cyclooctanol without the use of sacrificial co-reductant.

We have found that activity of free cobalt complexes increases in the order CoPorphyrin, CoSalen and CoPc, the latter being five times more active than the first one. CoPorphyrin after immobilization inside zeolite X increases its activity, whereas CoSalen and CoPc slightly decrease the activity. The catalytic activity of Mn and Fe complexes changes only to a small extent after encapsulation. The type of the macrocyclic ring and the type of metal determine the product yields and the selectivity to cyclooctanone and cyclooctanol which are strongly modified by encapsulation in the zeolite matrix. The results represent the first example of catalytic application of metallocomplexes encapsulated inside the zeolite structure for oxidation of hydrocarbons with dioxygen under high pressure and temperature without the use of sacrificial co-reductant. © 2004 Elsevier B.V. All rights reserved.

Keywords: Metalloporphyrins; Metallophthalocyanines; MetalloSalen; Immobilized metallocomplexes; Cyclooctane oxidation

1. Introduction

Increasingly restrictive regulations concerning environment protection induce progress in the technology of chemical processes. This is why there is a growing interest in homogeneous catalysts like enzymes. Enzymes are natural catalysts, well-known for their high selectivity, operating at mild temperatures but their use in an industrial environment is expensive and their handling and manipulation are rather difficult. On the other hand, the traditional heterogeneous catalysts are rather robust, can operate under more severe conditions, have generally good stability and are manufactured at relatively low costs. But in comparison with the enzymes their selectivity in most cases is significantly lower. The advantages of both systems could be combined and the disadvantages eliminated by the immobilization of homogeneous

catalysts e.g. enzymes on the surface of heterogeneous supports. The immobilization of metallocomplexes on different supports seems to be a good method to satisfy environmental demands and to obtain catalysts which preserve the properties of homogeneous systems, but are more stable and can be easily recovered.

Zeolite structures are attractive matrixes for immobilization of metal complexes which are known to be active in homogeneous catalysis. Especially the three-dimensional large pore zeolites X and Y have been studied as host lattices. When the encapsulated complex is too bulky to move away from a large cage or a channel crossing the term ship-in-a-bottle system applies [1–3]. The isolated complex immobilized in this way has special properties. It is unable to undergo transformations, which sometimes are deactivating processes in homogeneous catalysis. Moreover, when formed in the zeolite voids, the complex may have a unique configuration, which may differ from that existing in solution and acquire new catalytic properties. Finally, the zeolite surrounding may have a

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bearing on the selectivity in parallel reactions by influencing in a different way the transition states in question [4].

Most frequently inside the large pores of the zeolites metalloporphyrins and their analogues as phthalocyanines and Schiff bases [5–8] were prepared. They have been studied extensively as biomimetic catalysts for alkene epoxidation and alkane hydroxylation with variety of oxidants including hydrogen peroxide, hydroperoxides, iodosylbenzenes and hypochlorites [9–13]. There are only a few papers on oxidation of hydrocarbons with dioxygen in the presence of zeolite-encapsulated metallocomplexes as catalysts [14–16] and no papers on oxidation of hydrocarbons with these catalysts under high pressure and temperature.

In this work we describe the use of three macrocyclic complexes: metalloporphyrin, metallophthalocyanine and metalosalen encapsulated in NaX zeolite as catalysts in oxidation of cyclooctane with dioxygen in the absence of a reducing agent. The activity of such catalysts appears to be dependent on the character of the metal centre and the kind of the macrocyclic ligand. We have found that the immobilized metallocomplexes can be recycled and reused.

2. Experimental

2.1. Materials

Manganese, iron and cobalt cationic 5,10,15,20-tetrakis (*N*-methyl-4-pyridyl) porphyrins pentachloride (Mn(TMPyP)Cl₅, Fe(TMPyP)Cl₅ and Co(TMPyP)Cl₅) as well as phthalocyanine complex of cobalt were purchased from MidCentury Company. Cobalt salen [*N,N'*-bis (salicylidene)ethylenediamine] complex was synthesized according to the procedure described elsewhere [17]. The structures of these compounds are presented in Fig. 1.

Three series of samples were used: macrocyclic metal complexes, zeolite X exchanged with the same metals and

macrocyclic metal complexes encapsulated in zeolite X. The Na-form of zeolite X was subjected to ion-exchange in water solutions of the appropriate metal cations [18,19]. In the conditions used only Na⁺ ions present in the supercages were exchanged for the metal cations. After exchange, the zeolite was washed several times with water and dried. Iron and cobalt exchanged zeolites were coloured after the synthesis. The encapsulated complexes were prepared by the synthesis of zeolite X around these complexes. Because zeolite X is synthesized in the presence of metallocomplexes, their solubility in the synthesis mixture is an important issue. While the cationic metalloporphyrins are perfectly soluble in water, metallophthalocyanine and metalosalen complexes are water insoluble. In the latter case metallocomplexes were synthesized inside the faujasite structure using flexible ligand method during the reaction between the ion-exchanged zeolite X and the appropriate ligand. Moreover, after the encapsulation of the complexes, samples were additionally exchanged with NaCl solution to remove the metal cations which remained uncomplexed. Samples of zeolite X containing incorporated complexes were Soxhlet extracted with suitable solvents to remove the complexes at zeolite surface until extracting solutions were colourless indicating that only complexes encapsulated inside zeolite cages remained. After drying the samples were mixed with saturated solutions of NaCl and kept 1 h at room temperature to exchange uncomplexed M²⁺ cations.

2.2. Nitrogen physisorption measurements

BET surface areas and pore size distributions of the catalysts were calculated from nitrogen adsorption isotherms at 77 K in an Autosorb-1, Quantachrome equipment.

2.3. UV-vis spectroscopy

UV-vis spectroscopy was performed with a Shimadzu UV-vis 160 A double beam spectrophotometer with built-in recorder, using quartz cells of 1 cm optical path. Electronic spectra of the heterogenized metalloporphyrins were obtained in nujol mull between quartz plates.

2.4. X-ray diffraction

Powder X-ray diffraction patterns were recorded on a Siemens D5005 automatic diffractometer using Cu K α radiation (55 kV, 30 mA) selected by a graphite monochromator in the diffracted beam.

2.5. Infrared spectroscopy

FT-IR spectra were recorded on a Nicolet 800 spectrometer in KBr pellets over the range of 400–4000 cm⁻¹ under the atmospheric conditions.

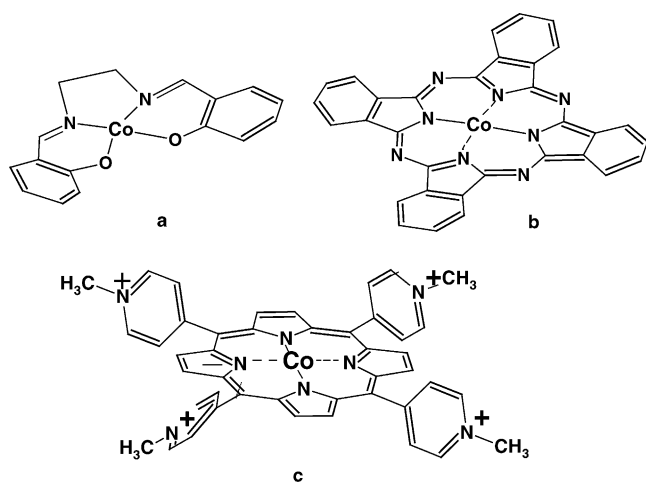


Fig. 1. Cobalt complexes entrapped inside zeolite NaX: (a) CoSalen; (b) CoPhthalocyanine; (c) CoPorphyrin.

2.6. Chemical analysis

The amounts of metal complexes encapsulated in zeolite matrix were determined by the elemental analysis and by subtracting the amount of metal complex left in the solutions after the synthesis of the catalysts as determined by UV–vis spectroscopy, from the amount taken for the synthesis. Atomic absorption spectra (AAS) were recorded on a Perkin-Elmer 3110 Spectrophotometer using a flame approach, after acid (HF) dissolution of known amounts of the zeolitic material.

2.7. Catalytic tests

The catalytic oxidation of cyclooctane, which simultaneously played the role of the reaction medium has been carried out in a stainless steel batch reactor system at the optimum temperature of 120 °C and under the air pressure of 10 atm, with the molar ratio of cyclooctane to oxygen set at 6.5. The Teflon lined reactor of 1 L volume equipped with magnetic stirrer was used.

In the typical experiment, the catalyst having the concentration of 3.3×10^{-4} M of metal complexes or its equivalent for the encapsulated metal complexes was introduced into the reaction mixture when the required reaction conditions were attained. After 6 h of reaction time the oxidation was stopped by immersing the hot reactor in a cold water bath. The products were analyzed by means of Agilent Technologies 6890N gas chromatograph equipped with Innowax (30 m) column.

3. Results and discussion

3.1. Catalysts characterization

BET measurements and spectroscopic characterization by UV–vis, AAS, FT-IR, XRD, of the synthesized catalysts have provided evidence that they are composed of the zeolite encapsulated metal complexes.

The contents of metal cations in the synthesized samples as measured using the atomic absorption spectroscopy amounted to: CoSalen/X 0.21% (w/w), CoPc/X 0.67% (w/w), Co(TMPyP)/X 0.15% (w/w), Fe(TMPyP)/X 0.15% (w/w) and Mn(TMPyP)/X 0.15% (w/w). Differences in loading of zeolites with porphyrins as compared to salen and phthalocyanine were due to different methods of synthesis.

The sorption properties of our catalysts were measured by means of BET technique (Table 1). The parent zeolite has the largest surface area and the largest total pore volume. Because the metalloporphyrins were encapsulated at the level of 0.15 wt.%, only a minor lowering of the surface area for the encapsulated macrocyclic complexes was observed. Also, pore volumes of heterogenized metalloporphyrins are only slightly lower than those measured for faujasite.

Table 1
Surface area and pore volume of catalysts

Sample	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
NaX	637.83	0.38
Mn(TMPyP)/NaX	594.08	0.36
Co(TMPyP)/NaX	602.79	0.36
Fe(TMPyP)/NaX	624.60	0.37
CoPc/NaX	405.60	0.32
CoSalen/NaX	448.50	0.28

Conversely in the case of encapsulated CoSalen and CoPc the surface area and the pore volume significantly decrease in comparison with parent zeolite. This may occur due to the synthesis method used for encapsulation of metal complexes. The zeolite synthesis method, which was applied in the case of metalloporphyrins allows to obtain more or less homogeneous distribution of the metal complexes in zeolite cages. In the method of flexible ligand, used for encapsulation of CoSalen and CoPc in faujasite, the gradient of concentration of encapsulated complexes between cages which are close to the external surface and internal cages appears.

The FT-IR spectra of the metal complexes heterogenized inside zeolite NaX are weak due to their low concentrations in zeolite matrix. Fig. 2 shows a comparison of the FT-IR spectra for NaX zeolite, CoSalen and CoSalen in zeolite NaX and Fig. 3 demonstrates similar FT-IR spectra of CoPhthalocyanine and CoPhthalocyanine in zeolite NaX. The zeolite broad band at 1050–950 cm⁻¹ dominates the region of the spectrum where the main bands characteristic for macrocycle can be

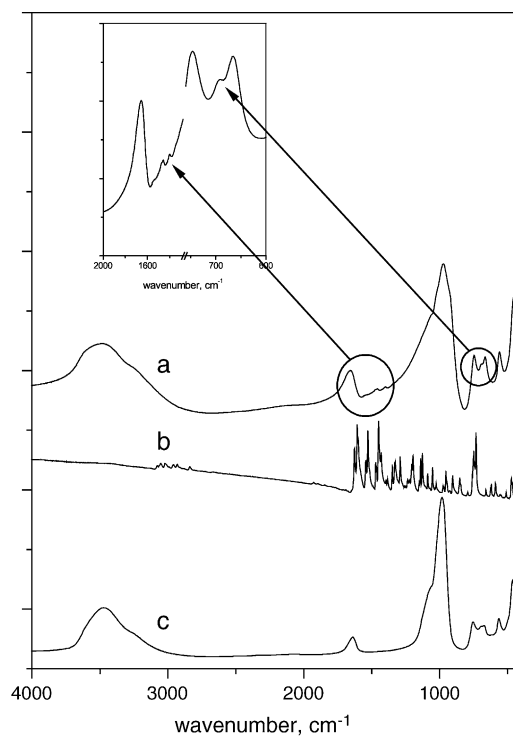


Fig. 2. FT-IR spectra of (a) CoSalen in zeolite NaX, (b) CoSalen, and (c) zeolite NaX.

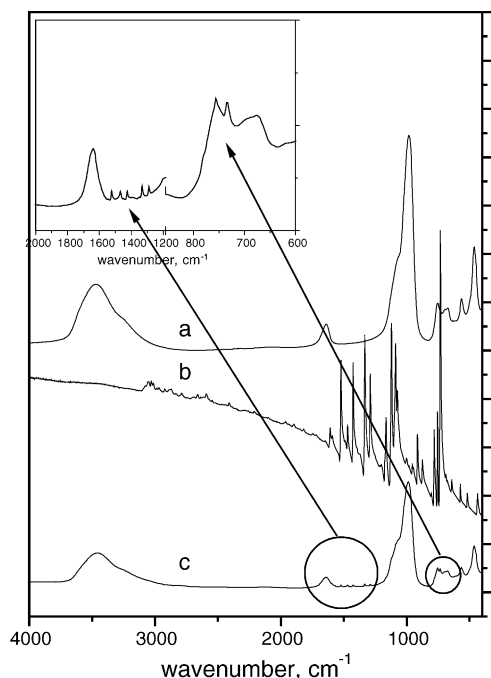


Fig. 3. FT-IR spectra of (a) zeolite NaX, (b) CoPc, and (c) CoPc in zeolite NaX.

observed. However, in the FT-IR spectra of the CoSalen in zeolite NaX and encapsulated CoPc we observed new characteristic bands in two regions between 1500 and 1350 cm^{-1} and between 700 and 670 cm^{-1} which are not present in zeolite NaX, as it is visible from comparison of the spectra shown in Fig. 2a and 2c, and Fig. 3a and 3c indicates the presence of cobalt Salen and phthalocyanine complexes inside the zeolite cages. The FT-IR spectra of encapsulated metalloporphyrins demonstrate no bands characteristic for these complexes. It is the result of the low level of encapsulated metalloporphyrin load, and of the method of synthesis of metallocomplexes in zeolite NaX, which guarantees their homogeneous distribution within zeolite cages. To verify whether the metalloporphyrin is incorporated into the zeolite structure, the sample containing about 10 wt.% of Co(TMPyP) in zeolite NaX was synthesized. The synthesized sample was dark-brown in colour. The sample was examined by FT-IR and again no characteristic IR vibrations were observed.

However, the UV–vis spectra confirm the inclusion of Co(TMPyP) complex within the zeolite cages (Fig. 4). The free Co(TMPyP) complex in water solution (Fig. 4a) and the same metalloporphyrin in nujol mull (Fig. 4c) have the Soret band in the range between 434 and 436 nm. After encapsulation of Co(TMPyP) complex into zeolite NaX a small blue shift of Soret band is observed (Fig. 4b) indicating that it is incorporated and was not modified during heterogenization.

In Fig. 5 the X-ray diffraction patterns of cobalt phthalocyanine encapsulated in zeolite matrix (a), cobalt salen in zeolite X (b), cobalt porphyrin in zeolite X (c) and parent zeolite NaX (d) are compared. No evidence of a collapse of the faujasite structure of the support and only small reduction in

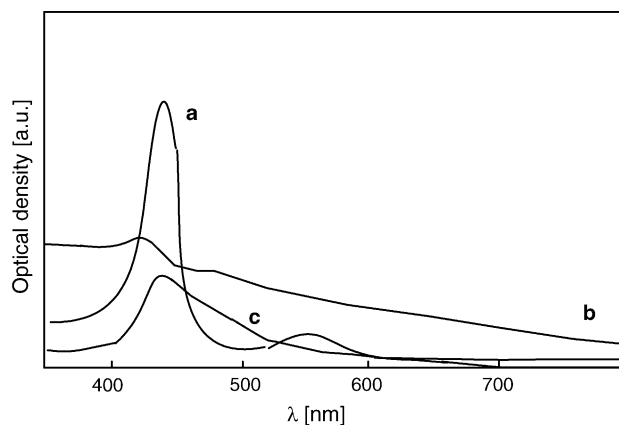


Fig. 4. UV–vis spectra of (a) Co(TMPyP) metalloporphyrin in water solution, (b) Co(TMPyP) metalloporphyrin encapsulated in zeolite NaX (prepared in nujol mull), and (c) Co(TMPyP) metalloporphyrin in nujol mull.

the intensities of the peaks were observed during the synthesis of the metallocomplexes in zeolite structure. The X-ray diffraction patterns of the Mn(TMPyP)/X and Fe(TMPyP)/X catalysts are not shown here, because their diffractograms are similar to the diffraction pattern of the Co(TMPyP)/X sample presented in Fig. 5c. It is also important to notice that the presence of metallocomplexes in zeolite reaction mixture did not hinder the synthesis of zeolite NaX.

3.2. Catalytic activity

For the initial studies on the catalytic activity of encapsulated metallocomplexes in the oxidation of cyclooctane with dioxygen cationic metalloporphyrins incorporated into zeolite NaX were selected to assess their catalytic properties in this reaction and compare with unsupported metallocomplexes. The oxidation of cyclooctane catalyzed by these catalysts produced cyclooctanone as the main product and cyclooctanol in small yield. Mn, Fe and Co are the most frequently used metals in oxidation reactions and those metals were chosen to synthesize cationic metalloporphyrins. All these studied catalysts are insoluble in reaction mixture. The catalytic results are given in Table 2 and the TON are plotted in Fig. 6. No reaction was observed in blank experiment when parent NaX zeolite was used as catalyst. As it can be seen from the data presented in Fig. 6, the catalytic activity of the system depends on the type of metal in macrocyclic rings. Among the cobalt compounds used in this reaction, cobalt exchanged zeolite shows some activity, the cationic cobalt porphyrin is two times more active, while the Co(TMPyP) encapsulated in NaX zeolite is the most efficient catalyst. Manganese exchanged zeolite shows some activity which is similar to manganese porphyrin Mn(TMPyP) but the activity of the Mn(TMPyP) entrapped in NaX zeolite is two times higher. It is interesting to notice that the encapsulated cobalt and manganese porphyrins are more efficient catalysts than their unsupported analogs. In the case of iron compounds, we have observed nearly the same activity for

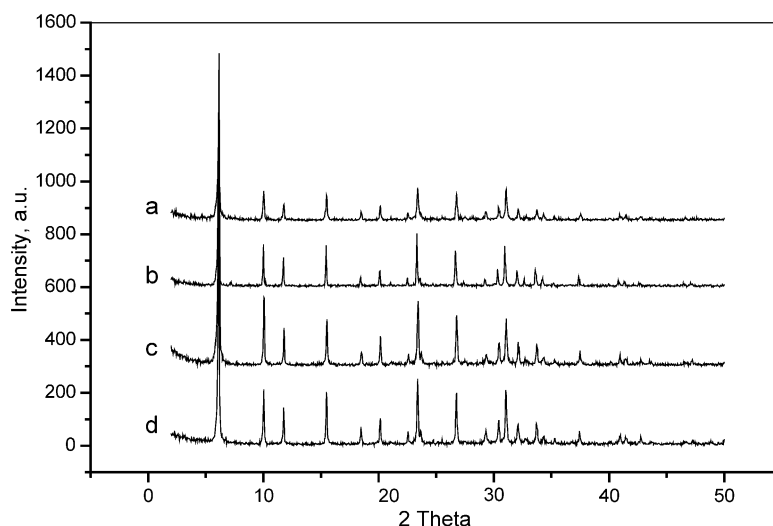


Fig. 5. X-ray diffraction patterns of (a) CoPc in zeolite NaX, (b) CoSalen in zeolite NaX, (c) Co(TMPyP) in zeolite NaX, and (d) zeolite NaX.

FeNaX, Fe(TMPyP) and Fe(TMPyP)/NaX catalysts. As regards the selectivities to the reaction products the cyclooctanone/cyclooctanol ratio varied in the narrow range 8–12.

The influence of macrocyclic ligands: phthalocyanine, salen and porphyrin on the catalytic oxidation of cyclooctane is shown in Table 3. All these ligands are tetradentate. Phthalocyanine and porphyrin are connected with the metal centre by four nitrogen atoms, while salen is bonded by two nitrogen atoms and two oxygen atoms. We have investigated three macrocyclic cobalt complexes: cationic porphyrin Co(TMPyP) and its two analogs – salen complex CoSalen and cobalt phthalocyanine CoPc and the same compounds incorporated into the NaX zeolite. Catalytic results (Fig. 7) reveal that free CoPc and CoSalen complexes are much more active

than Co(TMPyP). This may be due to the fact that the latter is insoluble in the reaction medium. In contrast, encapsulation of the Co(TMPyP) complex into the faujasite structure increases the catalytic activity in comparison with the free complex, activity of the other two macrocyclic complexes declines after encapsulation.

The present results clearly show that cobalt complexes are considerably more active than manganese and iron catalysts. This phenomenon may be connected with the fact that cobalt complexes form superoxo compounds with dioxygen which are stable in comparison with iron and manganese complexes [15] and therefore the mechanism of the oxidation reaction is different. In the case of cobalt salen complex in which cobalt is in divalent state the reaction starts by activation of dioxygen, being particularly active, whereas in the case of other cobalt complexes as well as iron and manganese complexes it is the activation of the hydrocarbon molecule by the axial ligand, which starts the chain reaction [20]. Thus, no sacrificial

Table 2

Oxidation of cyclooctane catalyzed by different cationic metalloporphyrins, zeolite X exchanged with the same metals and cationic metalloporphyrins encapsulated in zeolite

Catalyst	Cyclooctanone TON ^a	Cyclooctanol TON ^a	C-one + C-ol TON ^a	Ratio C-one/C-ol
NaX	–	–	–	–
CoNaX	1980	220	2200	9.0
Co(TMPyP)	4180	440	4620	9.5
Co(TMPyP)/NaX	9020	1100	10120	8.2
MnNaX	2200	220	2440	10.0
Mn(TMPyP)	2200	220	2440	10.0
Mn(TMPyP)/NaX	4180	440	4620	9.5
FeNaX	2420	220	2640	11.0
Fe(TMPyP)	2640	220	2860	12.0
Fe(TMPyP)/NaX	2200	220	2440	10.0

^a Mol product \times mol catalyst⁻¹ h⁻¹ (mole catalyst means mole metalloporphyrin in homogeneous system or mole of metalloporphyrin in heterogeneous system or the same amount of metal contained in metalloporphyrin in the case of metal exchanged zeolite X).

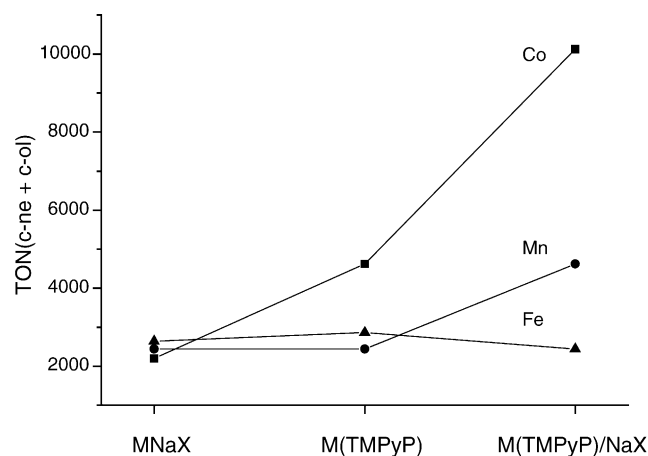


Fig. 6. The influence of type of metal on the catalytic oxidation of cyclooctane.

Table 3
Oxidation of cyclooctane catalyzed by different cobalt macrocyclic complexes and these complexes encapsulated in zeolite X^a

Catalyst	Cyclooctanone TON ^a	Cyclooctanol TON ^a	C-one + C-ol TON ^a	C-one/C-ol ratio
Co(TMPyP)	4180	440	4620	9.5
Co(TMPyP)/NaX	9020	1100	10120	8.2
CoSalen	13641	1760	15401	7.7
CoSalen/NaX	7698	660	8358	11.7
CoPc	21778	2640	24418	8.2
CoPc/NaX	17821	5720	23541	3.1
CoPc/NaX ^b	16910	4920	17402	3.4

^a Mol product \times mol catalyst⁻¹ h⁻¹ (mole catalyst means mole metalloporphyrin in homogeneous system or mole of metalloporphyrin in heterogeneous system or the same amount of metal contained in metalloporphyrin in the case of metal exchanged zeolite X).

^b Catalyst recycled and reused.

reductant is necessary. Additionally, it has been shown that the zeolite matrix behaves like an electron-withdrawing substituent [4]. Thus, the encapsulation depletes electron density at the metal centre. This enhances the binding of dioxygen molecules at the metal centre and may change the catalytic properties of the encapsulated macrocyclic complexes in oxidation reaction in comparison with free complexes. Moreover, geometric constraints inside the zeolite cavities distort the geometry of the complex. The large cavity in zeolite X has the diameter of 1.3 nm. It can easily accommodate the molecule of metallosalen of the diameter 1.1 nm and metalloporphyrin of the diameter 1.2 nm whereas the molecule of metallophthalocyanine with the diameter of 1.3 nm is slightly squeezed. This has a dramatic influence on the selectivity. In the case of CoSalen/NaX the selectivity to cyclooctanone increases, whereas for CoPc/NaX it considerably decreases. The encapsulated catalyst CoPc in zeolite NaX showing highest activity was recovered and reused. The results presented in Table 3 indicate that this catalyst gave still quite high yields. Thus, it seems that encapsulated metal complexes are promising catalysts for the development of a continuous process.

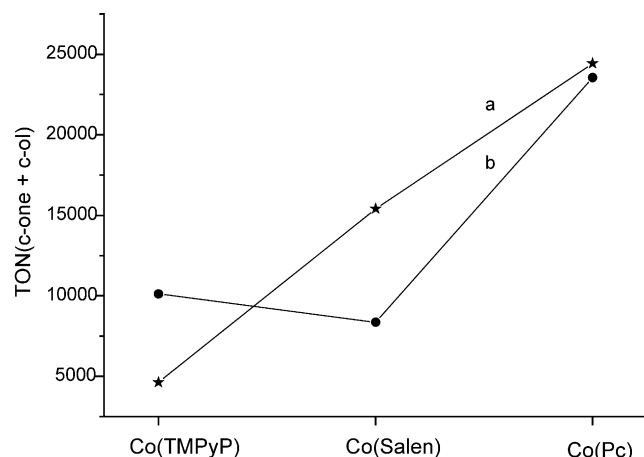


Fig. 7. The influence of macrocyclic ligand on the catalytic oxidation of cyclooctane in the presence of (a) free metal complexes, and (b) metal complexes encapsulated in zeolite NaX.

4. Conclusions

In this work, we described the use of different cobalt, iron and manganese macrocyclic compounds free and encapsulated in zeolite NaX as catalysts for cyclooctane oxidation. The catalytic results show that the choice of the metal centre and macrocyclic ligand influences the yields of the products: cyclooctanone and cyclooctanol and the selectivity. All catalysts show selectivity towards the formation of cyclooctanone. These results represent the first example of catalytic application of encapsulated metal complexes in zeolite structure for oxidation of hydrocarbons which utilizes dioxygen as the oxidant under high pressure and temperature and in which the sacrificial co-reductants are not required. The encapsulated complexes could be recycled and reused with small changes in catalytic activity.

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