Rate enhancement of oxidation reactions by the encapsulation of metal phthalocyanine complexes

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Iron phthalocyanine (FePc) and cobalt phthalocyanine (CoPc) as free complexes as well as encapsulated in zeolite-Y (FePc-ZeY and CoPc-ZeY) have been studied as catalysts in mild, aerobic oxidation of hydroquinone. A remarkable rate enhancement was observed with the encapsulated catalysts, especially in the case of the encapsulated cobalt phthalocyanine, where the encapsulated complex was a good, active oxidation catalyst, while its homogeneous analogue was completely inactive. The site isolation effect is responsible for the observed rate enhancement. The solvent effect was also studied in the case of free complexes and encapsulated catalysts.

Keywords: iron phthalocyanine, cobalt phthalocyanine, encapsulated catalysts, oxidation reactions, oxidation of alkenes, rate enhancement, oxidation with molecular oxygen

1. Introduction

The importance of oxidation reactions in the synthesis of fine chemicals and the recent development in the field of encapsulated catalysts has emphasized the application of the *ship-in-a-bottle* type catalysts for oxidation reactions [1,2]. Molecular oxygen is an attractive oxidant both from an economic and environmental point of view. Unfortunately, molecular oxygen is more difficult to activate than other oxidants, such as iodosylbenzene or peroxides [3,4]. Macrocyclic metal complexes, however, have recently been reported as dioxygen activating catalysts [5]. Mild and selective oxidation processes, involving multistep electron transfer between Pd(0)/Pd(II), hydroquinone/benzoquinone and the oxidized/reduced form of macrocycles were developed [5b,5c].

The oxygen activating macrocyclic metal complexes, however, have some disadvantages. They have very poor solubility in most organic solvents, they can dimerize, and they are susceptible to self-degradation. One way to avoid these problems is to heterogenize these metal macrocycles. Using this approach the stability can be increased and the problem of solubility can be overcome. Our basic goal was to find easily manageable and recyclable catalysts for the activation of molecular oxygen for the above mentioned, mild and selective oxidation process.

The physical entrapment of the macrocyclic metal complexes into a zeolite supercage could result in a favorable combination of heterogeneous and homogeneous catalysis. In the ideal case, this would combine the high selectivity, controllability and activity of the homogeneous catalysts with the easy handling of the heterogeneous catalysts. Additionally the zeolite host can provide a stabilizing effect, since it can prevent the catalyst deactivation by hindering the formation of peroxo- and μ-oxo-bridged species.

Metal macrocycles encapsulated in zeolites can be synthesized in three different ways [1,6]: (i) in the *flexible ligand* or *intrazeolite complexation* method the ligand is allowed to diffuse into the pores of a metal-exchanged zeolite, and on complexation with a metal ion inside the pores it becomes too large to exit; (ii) the *template synthesis* or *intrazeolite synthesis* method involves diffusion of the ligand precursors into the zeolite pores where they react to give the ligand, which coordinates to the intrazeolite metal ion; and (iii) the basis of the *zeolite synthesis* method is “to build the bottle around the ship” by crystallization of the zeolite around a metal complex which serves as a template for zeolite synthesis. The latter method is restricted to metal complexes, e.g., metal phthalocyanines (figure 1) that are stable under the relatively harsh conditions of the zeolite synthesis.

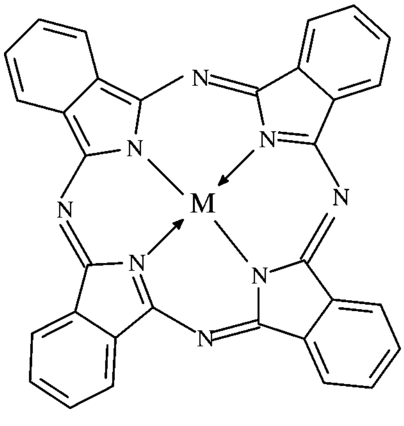


Figure 1. Metal phthalocyanine complexes (M = Fe or Co).

In our previous work the encapsulated iron phthalocyanine and cobalt salophen catalysts were synthesized by the template synthesis method and they were applied in aerobic oxidation reactions [7,8]. Several advantages – stability, easy separation, recyclability – of the encapsulated catalyst over the homogeneous non-encapsulated metal macrocycles were found. In some cases a remarkable rate enhancement was observed using the heterogenized catalysts [8]. In this communication we have focused on the latter feature and report on rate enhancements by encapsulated iron and cobalt phthalocyanines (figure 1).

2. Experimental

2.1. Materials

Cobalt(II) acetate tetrahydrate, 1,2-phenylenediamine (98%), 1,2-dicyanobenzene (98+%), iron(II) phthalocyanine (FePc), cobalt(II) phthalocyanine (CoPc), salicylaldehyde and NaY zeolite were purchased from Aldrich and used as received.

2.2. FePc-ZeY and CoPc-ZeY catalysts

Zeolite-encapsulated iron phthalocyanine (FePc-ZeY) and cobalt phthalocyanine (CoPc-ZeY) catalysts were synthesized by the intrazeolite synthesis method. Fe^{2+}- or Co^{2+}-containing zeolites were prepared by ion exchange for 48 h at room temperature, using 6 g of NaY and 250 ml of 1 N $FeSO_4 \cdot 7H_2O$ or 0.5 N $Co(OAc)_2 \cdot 4H_2O$, respectively. The ion-exchanged zeolites were filtered, washed with deionized water until no iron or cobalt was observed in the filtrate and dried overnight at 250 °C. The Fe^{2+}- and Co^{2+}-containing zeolites were mixed with 6 g of 1,2-dicyanobenzene and 15 ml decalin, and heated to 250 °C. The mixture was stirred for 4 h at this temperature, then cooled to room temperature. The product was washed with acetone to remove the excess of the precursor. The surface complex was removed by Soxhlet extraction with pyridine for 48 h. The material was washed with acetone to remove the pyridine and, finally, dried overnight at 70 °C.

2.3. Catalyst characterization

The washing and extraction procedure removed all of the remaining unchanged precursor and the complexes from the catalyst surface. The presence of the encapsulated metal complexes was demonstrated by the FT-IR spectra [9,10]. FT-IR spectra were taken from the homogeneous complexes as well as from the encapsulated ones. These spectra confirm the structure of the complexes and that there were no uncomplexed ligands in the zeolite. The uncomplexed metal ions were re-exchanged, using saturated NaCl solution. Thus all of the residual metal ions are associated with metal complexes, so the analysis of iron or cobalt contents allowed the determination of the amount of the metal complexes in the zeolite. The ICP-AES method was used to determine the amount of complex in the zeolite. The amount of complex determined before and after the reaction was within the experimental error. In this way it was found that the concentration of the active complex in the FePc-ZeY catalyst was 0.02 $mmol\,g^{-1}$, while it was 0.4 $mmol\,g^{-1}$ in the CoPc-ZeY. The nitrogen content was not suitable for the determination of the amount of metal complexes because of the presence of uncomplexed phthalocyanine. Additionally, we have used Mössbauer spectroscopy in the case of FePc-ZeY to prove the planarity of the structure [13].

2.4. Oxidation reactions

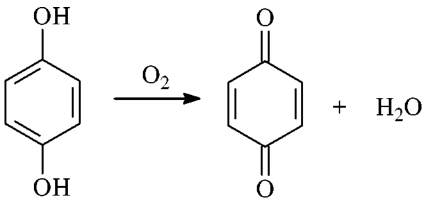
The oxidation reactions were carried out in a closed flask using an oxidation apparatus, and the glass reactor was shaken in a vortex manner [11]. The reactions were performed at room temperature under atmospheric pressure of molecular oxygen and the oxygen uptake was followed by a pressure transducer.

Oxidation of hydroquinone in acetic acid catalyzed by encapsulated complexes (FePc-ZeY or CoPc-ZeY). 250 mg of hydroquinone (2.27 mmol) and 0.1 g encapsulated catalysts (0.002 mmol FePc or 0.04 mmol CoPc, respectively) were used in 5 ml of acetic acid.

Oxidation in different solvents catalyzed by free or encapsulated complexes. 250 mg of hydroquinone (2.27 mmol) and 0.053 mmol metal macrocycle (FePc or CoPc) or 0.1 g encapsulated catalysts were used in 5 ml acetic acid, N,N-dimethylformamide or dichloromethane, respectively.

3. Results and discussion

It was found earlier [5] that the free iron phthalocyanine complex was an active catalyst in the oxidation of hydroquinone to benzoquinone:



(1)

3.1. Rate enhancement by encapsulation of iron phthalocyanine in NaY zeolite

The activity of the encapsulated FePc catalyst was compared with the performance of the free FePc complex in the aerobic oxidation reactions. The oxygen uptake for the oxidation of hydroquinone to benzoquinone based on the iron phthalocyanine content on both catalysts is shown in figure 2.

Two oxygen uptake curves for the oxidation of hydroquinone to benzoquinone with the two catalysts (figure 2) show different shapes. With free iron phthalocyanine the

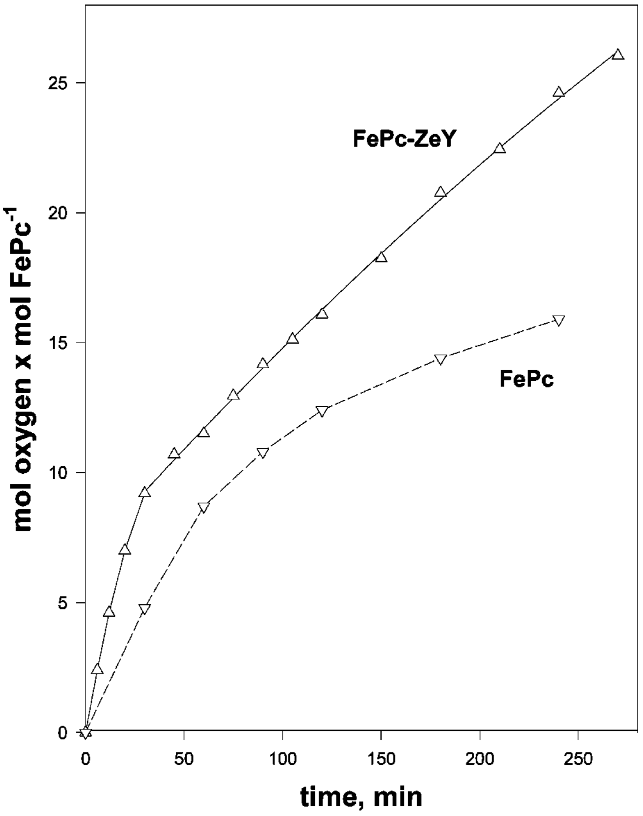


Figure 2. Specific oxygen uptake values (mol-O_2 mol-FePc^{-1}) for the oxidation of hydroquinone catalyzed by iron phthalocyanine and zeolite encapsulated iron phthalocyanine catalysts in acetic acid.

Table 1
Initial rate values (mol-O_2 mol-MPc^{-1} h^{-1}) and the TON (mol-O_2 mol-MPc^{-1}) after 4 h for oxidation of hydroquinone to p-benzoquinone catalyzed by metal phthalocyanines in acetic acid.

Catalyst	Initial rate	TON (after 4 h)
FePc	9.7	16
FePc-ZeY	24.0	24.0
CoPc	0	–
CoPc-ZeY	10.4	6.0

rate of the oxidation is gradually decreasing with increasing time. Using the encapsulated catalyst, however, higher oxygen uptake rate was observed at the beginning but after a certain period the rate decreased. This smaller rate, however, remained almost constant for a relatively long period of time. This phenomenon was characteristic for all of the encapsulated catalysts, studied by us.

On the basis of the initial slopes specific initial reaction rate values were calculated for the oxidation of hydroquinone to benzoquinone (table 1, entries 1 and 2).

The specific activity of the encapsulated catalysts was about two and a half times higher than the activity of the free complexes. There are several different ideas to explain this rate enhancement. One of the possible explanations is based on the fact that the approximate diameter of the iron phthalocyanine molecule is about 1.32 nm, while zeolite Y has a three-dimensional pore system with about 0.74 nm channels that open up to supercages 1.2 nm in diameter [12]. It means that the size of the iron phthalocyanine molecule is a little bit larger than the diameter of the supercage in the Y zeolite, i.e., the encapsulated iron phthalocyanine complex must have a curved shape in the supercage of the zeolite [9,13]. This distortion of the molecule can cause the increased catalytic activity observed.

To check this idea we studied the structure of the encapsulated iron phthalocyanine complex by Mössbauer spectroscopy [14]. We found that, in spite of the distortion of the molecule, the four nitrogens surrounding the central iron atom have a flat (planar) structure. This finding suggests that the enhanced activity of the encapsulated FePc may not be due to distortion of the molecule.

Another likely explanation is that the encapsulated catalyst has a higher activity than the free homogeneous catalyst because the former is not deactivated. The formation of μ-oxo dimers may be responsible for the decreased catalytic activity of the free FePc. The μ-oxo dimers can be formed easily in the case of the free complexes during the oxidation reaction [15]. The encapsulation, however, prevents the formation of these dimers and the catalytic activity is maintained (site isolation effect).

3.2. Rate enhancement by encapsulation of cobalt phthalocyanine in NaY zeolite

Encapsulation of CoPc was carried out by the template synthesis method. It was found that the free cobalt phthalocyanine complex was completely inactive in the oxidation of hydroquinone to benzoquinone in dichloromethane, N,N-dimethylformamide, or acetic acid. On the other hand, the encapsulated CoPc-ZeY showed a good activity in the corresponding oxidation in acetic acid and was stable during the reaction (figure 3).

On the basis of the initial slopes the initial reaction rate values were calculated (table 1, entries 3 and 4).

It is likely that dimerization is responsible for the lack of activity of free CoPc. Encapsulation would prevent this deactivation by site isolation. This very interesting observation, that the encapsulated catalyst (CoPc-ZeY) is active, while the free complex (CoPc) showed no activity at all, has not been emphasized in the literature, so far. There is only one example in the literature [16], which is referring to a similar observation. However, that work was done in gas phase using a microcatalytic pulse reactor and the observation was attributed to the lack of solvent. Since we could prove that the free CoPc complex was not active in homogeneous conditions in liquid phase either, their explanation "The faujasite matrix seems to act in a similar manner as a solvent or support" may not be correct.

Zeolites have been considered as solid solvents by other authors, too, and several of their characteristics were described using solvent effects as an analogy [17]. Our results show that the CoPc catalyst is also inactive in var-

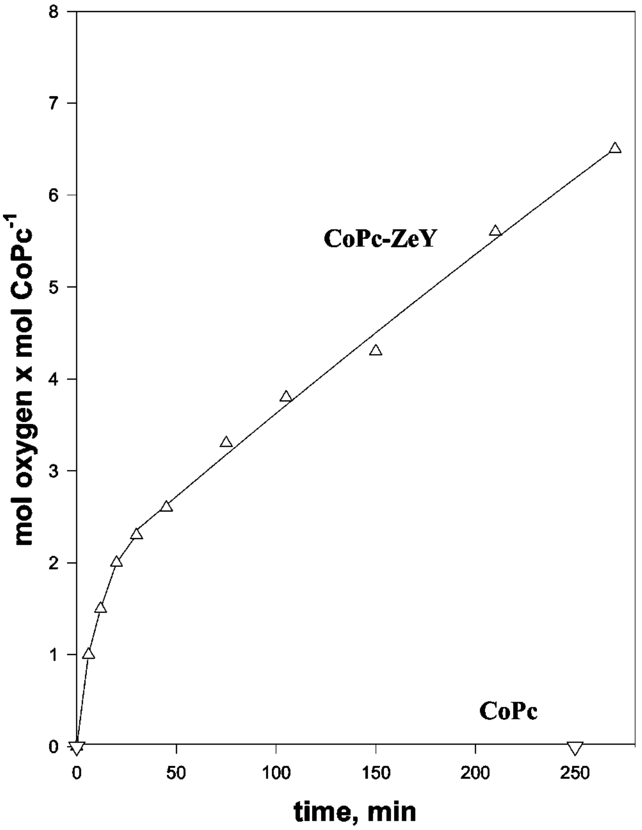


Figure 3. Specific oxygen uptake values (mol-O_2 mol-CoPc^{-1}) for the oxidation of hydroquinone catalyzed by cobalt phthalocyanine catalysts in acetic acid.

ious solvents (N,N-dimethylformamide, dichloromethane and acetic acid). The experimental data observed by us are therefore not consistent with the assumption that the zeolite matrix serves as a solid solvent for the CoPc. The likely explanation is that the encapsulation prevents the formation of inactive μ-oxo dimers and thus a stable and active catalyst is obtained.

3.3. The effect of solvent on the rate of the oxidation of hydroquinone

We also studied the effect of solvent in the aerobic oxidation of hydroquinone to benzoquinone using both free and zeolite encapsulated iron phthalocyanine catalysts. Acetic acid (protic solvent), N,N-dimethylformamide (a coordinating solvent) and dichloromethane (weakly coordinating solvent) were used. The observed results are shown in figure 4 for the free complexes and in figure 5 for the encapsulated ones.

The calculated initial rates in the different solvents are shown in table 2. It was found that the initial rate values are similar in different solvents but the rate differences increase during the course of the reaction.

It is known that the FePc-catalyzed O_2 oxidation of hydroquionone to benzoquinone most likely occurs via heterogeneous catalysis, because iron phthalocyanine has a low solubility in most organic solvents and exists as a finely divided powder in the reaction mixture. The encapsulated catalyst, however, consists of molecularly dispersed complexes in the zeolite supercages. The similar initial rates show that the solubility difference does not play an important role in this case.

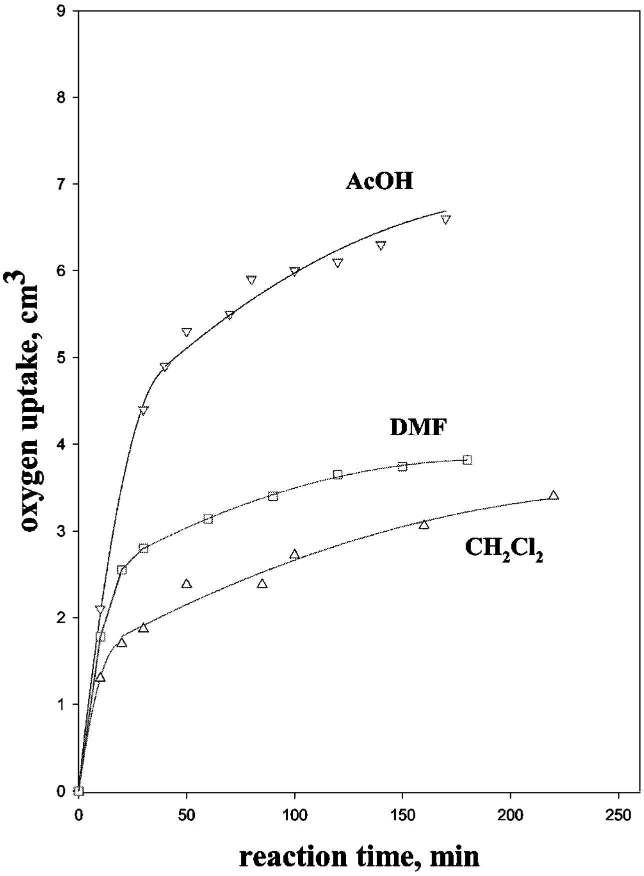


Figure 4. Oxygen uptake values for the oxidation of hydroquinone catalyzed by iron phthalocyanine complexes in different solvents.

In spite of the similar initial rates the reaction profiles are quite different in different solvents. The rate decrease was small in acetic acid while it was the largest in dichloromethane. The trend was similar in the case of the encapsulated catalysts, too, but the effect was more pronounced.

It is known that polar reaction products can solvate the inner cages of the zeolites and more polar solvents are necessary to remove these products from the adsorption sites. In this respect the acetic acid is the best solvent while dichloromethane is not so good for removing p-benzoquinone from the zeolite cages.

The desorption process is governed by the rate of the intraparticle diffusion and this phenomenon is responsible for the special shape of the reaction curve in the case of the encapsulated catalysts. Namely, after an initial period, the reaction rate decreases but remains constant for a relatively long period of time. The extent of the initial period depends on the solvent. It is more pronounced in the case of dichloromethane, it is smaller in N,N-dimethylformamide and it is smallest in acetic acid.

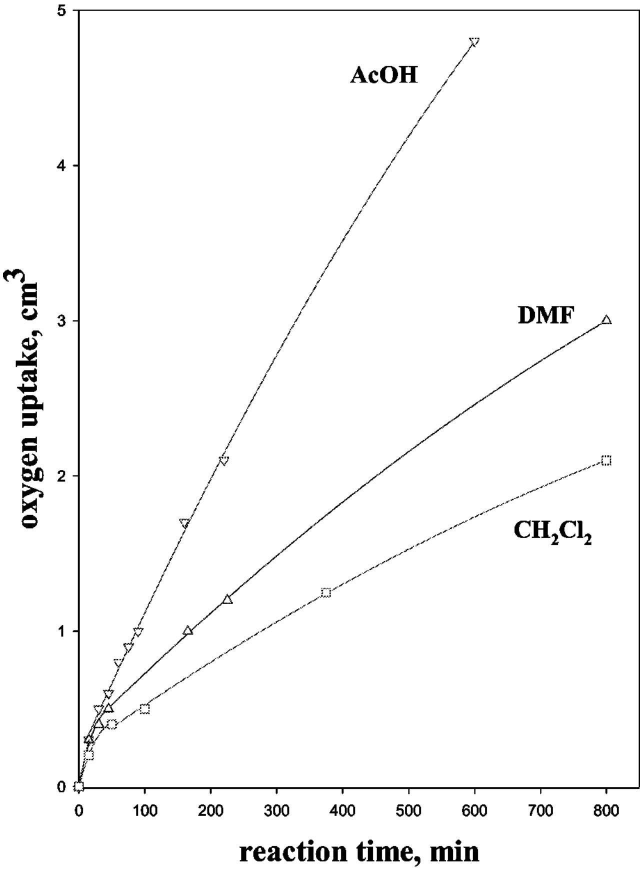


Figure 5. Oxygen uptake values for the oxidation of hydroquinone catalyzed by encapsulated iron phthalocyanine complexes in different solvents.

Table 2
Initial rate values (mol-O_2 mol-FePc^{-1} h^{-1}) for oxidation of hydroquinone to p-benzoquinone in different solvents.

Catalyst	Initial rates in		
	Acetic acid	Dichloromethane	N,N-dimethylformamide
FePc	9.7	5.8	8.0
FePc-ZeY	24.0	16.0	24.0

4. Conclusions

(1) Encapsulated iron and cobalt phthalocyanines show a higher reaction rate in the oxidation of hydroquinone to benzoquinone than the corresponding free complexes studied.

(2) The most significant rate enhancement was observed with the encapsulation of the CoPc complex. The heterogenization of this complex produced an active catalyst, while its homogeneous counterpart was completely inactive.

(3) The experimental data can be explained by the effect of site isolation, which can prevent the formation of μ-oxo dimers in the oxidation reactions.

(4) The oxygen uptake rates were the highest in acetic acid and solvent effects were similar in the case of free complexes and encapsulated catalysts.

Acknowledgement

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