

Cyclohexane oxidation with tertiary-butylhydroperoxide catalyzed by iron–phthalocyanines homogeneously and occluded in Y zeolite

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Abstract

Oxidation of cyclohexane to cyclohexanol and cyclohexanone at room temperature is achieved on iron phthalocyanine complexes encapsulated in Y zeolites with tertiary butyl hydroperoxide as oxygen atom donor. Sorption measurements show a high preference of the catalyst for polar reagents and products like acetone, cyclohexanol, cyclohexanone and tertiary butyl hydroperoxide. Therefore, the mode of addition of peroxide and the use of solvent have a strong influence on the reaction rate. A fed-batch type set-up with slow addition of the peroxide to the reaction mixture is proven to be the best system, minimizing the decomposition reaction of the peroxide and maximizing its selective oxidation reaction. Conversion of cyclohexane with iron–phthalocyanines encapsulated in Y zeolites is relatively high (up to 25%) with efficiencies between 40 and 10% and high selectivities for cyclohexanone (95%). Cyclohexanol is converted up to 70% with efficiencies around 70%, because the alcohol function is more sensitive to oxidation and sorption effects favor cyclohexanol compared to cyclohexane. The iron–phthalocyanine Y zeolites are regenerable for both reactions. Activities obtained by the zeolite encapsulated iron–phthalocyanines are higher than the homogeneous complexes which are oxidatively destroyed under reaction conditions and therefore not regenerable.

Keywords: Iron; Phthalocyanine; Zeolite Y; Oxidation; Cyclohexane; Cyclohexanol; Hydrophilicity; Peroxide

1. Introduction

Since the catalytic and selective formation of carbon–oxygen bonds is often accompanied by the formation of free organic radicals [1], selectivity is low and there is a need for catalysts

which control the fate of formed radicals or prevent their formation. Transition metal porphyrins and phthalocyanines are potential catalysts which fulfil these requirements. With these complexes, many authors [1] have tried to make a surrogate of the active entity of cytochrome P-450. However, without a proper mimic of the protein, rapid deactivation and poor selectivity results. Immobilizing these complexes on mi-

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porous solids such as zeolite Y can solve these problems [2–8]. Up to now, iodosobenzene has been used to oxidize alkanes with these zeolite encapsulated complexes [9–15]. However, as a result of the low solubility of iodosobenzene, and pore blockage by its self-oxidation product iodoxybenzene, only low turn-overs are realized [9–13]. With tertiary butyl hydroperoxide (*t*-BHP), an industrially more appropriate oxygen source [16], much higher turn-over values are obtained [17–22], provided that unchelated transition metal is absent. Recently, we [23] succeeded in making a higher order mimic of cytochrome P-450 [24] by embedding the iron-phthalocyanine Y catalyst in a hydrophobic membrane, which imitates the phospholipids of eukaryotic cells. These catalysts have been shown to be superior to other mimics. In this paper, we report the oxidation of cyclohexane, the major feed stock for the production of ϵ -caprolactam or adipic acid via cyclohexanone [25], with iron phthalocyanine Y (FePcY) catalysts. We will show that the reactions on FePcY are directed by the hydrophilic nature of the catalyst favoring alcohol oxidation and suppressing alkane oxidation. Moreover, the zeolite cage protects the complex against oxidative destruction which makes the heterogeneous system more stable than the homogeneous complex.

2. Experimental

Commercial NaY with a silicon to aluminium ratio of 2.47 is obtained from Zeocat. Cyclohexane (+99%), cyclohexanol (+99%), cyclopentanol (+99%) and acetone (p.a.) are purchased from Janssen Chimica; 1,2-dicyanobenzene (DCB) (+98%), dimethylformamide (99%) (DMF), *t*-BHP (70% in water) and ferrocene (98%) from Aldrich.

Vis–NIR absorption and FT-IR spectroscopy were performed on a CARY 17 and a Nicolet 730, respectively.

The catalytic reactions are carried out in the

liquid phase in a batch reactor with continuous stirring at room temperature (298 K), atmospheric pressure, with *t*-BHP (200 mmol) as mono oxygen atom donor, acetone (50 ml) as solvent, 0.5 g FePcY or 0.025 g FePc catalyst and 50 mmol substrate. Identification and quantification of products occurs by GC analysis on a 50 m CP-Sil-88 CB capillary column from Chrompack, using the appropriate sensitivity factors for an FID detector.

3. Results and discussion

3.1. Synthesis

Iron phthalocyanine Y zeolites are synthesized by the solid state adsorption of ferrocene (0.575 g, 1 molecule per supercage) on 5 g NaY dried at 523 K under nitrogen atmosphere [17]. Subsequently, the ferrocene-loaded zeolite is mixed with 3.15 g 1,2-dicyanobenzene (a twofold excess) and placed in a Teflon-lined autoclave. The autoclave is heated at 453 K for 24 h. The blue–green solid obtained is Soxhlet extracted with acetone, dimethylformamide and again with acetone, until a colorless extract is obtained. The extractions remove phthalocyanines from the outer surface of the zeolite, and unreacted reactants and intermediates from the crude catalyst. The final catalyst is air dried at 343 K.

3.2. Characterization

The resultant blue–green catalyst has an X-ray powder diffraction pattern consistent with zeolite Y without any pattern from crystalline phthalocyanines. UV–Vis and IR spectra confirm that this catalyst contains a mixture of free-base and iron phthalocyanines. UV–Vis spectroscopy was used for the determination of the amount of intracrystalline phthalocyanines, after the dissolution of the zeolite in concentrated sulfuric acid (0.1 g of catalyst in 100 ml of concentrated sulfuric acid for 4 h). The FePcY

catalysts synthesized by the procedure explained above have about 1.14 FePc complexes and 3.2 Pc molecules per unit cell. Therefore, the most of the phthalocyanines are without an iron ion incorporated into the macrocycle. On the other hand, no residual transition metal is left in the zeolite, which is confirmed by chemical analysis (AAS). Consequently, the catalytic results are not altered by unchelated iron.

3.3. Catalytic experiments

3.3.1. Fed-batch as the most practical reaction mode

It has been shown that FePcY behaves formally and mechanistically like cytochrome P-450 [23]. Cytochrome P-450 is a well-known oxygenation enzyme, which has a hydrophobic environment around its active site [24]. Therefore, it can stop the oxidation of alkanes at the stage of the alcohol. It is proposed that the high activity of enzymes is due to their ability to concentrate the reactants near the active site [26,27]. Protein polarity is the driving force for this process. Similarly, reaction rates in zeolites are determined by the concentration of the reactants in the interior space [28,29]. In the case of alkane oxidation with zeozymes (ZEOLite and enZYME), where reactants and products with strongly different polarity are present, preferential adsorption is expected to influence the reaction. Since aluminium rich faujasites have a hydrophilic nature [30], it is anticipated that polar reactants will be preferentially adsorbed compared to apolar molecules like alkanes. This is clearly shown in Table 1 where partition coefficients (K) in cyclohexane solvent are given for the FePcY zeozyme. K is a proportionality coefficient between the concentration of tracer adsorbed in the catalyst and the concentration of tracer in the bulk solution. The K values indicate the preference for a tracer compound to sorb in the catalyst compared to cyclohexane. The determination occurs according to the method published by Lin and Ma [31]. The catalyst is found to have a stronger affinity

Table 1

Adsorption of tracer compounds on FePcY catalyst with cyclohexane as carrier

Tracer compound	K^a	Tracer compound	K
cyclohexanol	> 30	acetone	22
cyclohexanone	26	n-hexane	0.9
<i>t</i> -butanol	15	n-decane	0.7
<i>t</i> -BHP	> 30	benzene	4.3

^a $Q = KC$ where Q is the concentration of adsorbed tracer compound (mol m^{-3}); C is the concentration of tracer compound in solution (mol m^{-3}). K is the proportionality constant and represents a partition coefficient.

(factor 20) for polar compounds such as acetone, cyclohexanone, cyclohexanol, *t*-BHP and *t*-butanol than for cyclohexane. n-Alkanes have a lower, and benzene a fourfold greater, affinity for the catalyst. Therefore, preliminary experiments (Tables 2 and 3) were performed to study the influence of the mode of addition of the polar peroxide to the reaction mixture and the use of acetone as a solvent. The two competitive reactions, i.e. the selective oxidation of cyclohexane with *t*-BHP (I) and the decomposi-

Table 2

Conversion of cyclohexane to cyclohexanol and cyclohexanone with 0.5 g FePcY catalyst

Time (h)	(A)	(B)	(C)	(D)
<i>Conversion (%)</i>				
5	2.2	3.1	6.5	5.7
15	15.2	9.7	13.8	15.8
50	15.9	14.0	16.6	21.8
150	15.9	19.1	19.9	31.8
<i>Efficiency^a (%)</i>				
5	18	48	41	88
15	17	42	29	61
50	15	32	23	36
150	13	25	13	32

Conditions; 298 K, 0.1 MPa, 50 ml acetone, 50 mmol cyclohexane and 200 mmol *t*-BHP. Reaction modes: (A) batch; (B) fed-batch with addition of *t*-BHP (at a rate 2.19 mmol h^{-1} , achieved by diluting the peroxide (1/1) with the solvent acetone); (C) fed batch with addition of *t*-BHP (4.38 mmol h^{-1}); (D) fed-batch without solvent and with addition of *t*-BHP (4.38 mmol h^{-1}).

^a The efficiency is defined as the amount of peroxide used for the selective oxidation of cyclohexane compared to the total amount of peroxide converted.

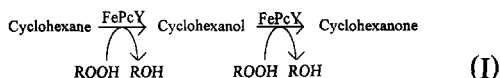
Table 3
Conversion of cyclohexanol to cyclohexanone with 0.5 g FePcY catalyst

Time (h)	(A)	(B)	(C)	(D)
<i>Conversion (%)</i>				
5	30.8	12.6	12.5	17.5
15	35.2	17.8	17.5	26.6
50	42.1	22.9	45.6	40.8
150	67.0	44.1	64.4	71.3
<i>Efficiency^a (%)</i>				
5	88	100	100	100
15	85	100	100	100
50	79	100	100	92
150	75	100	91	75

Conditions; 298 K, 0.1 MPa, 50 ml acetone, 50 mmol cyclohexanol and 200 mmol *t*-BHP. Reaction modes: (A) batch; (B) fed-batch with addition of *t*-BHP (at a rate 2.19 mmol h⁻¹, achieved by diluting the peroxide (1/1) with the solvent acetone); (C) fed batch with addition of *t*-BHP (4.38 mmol h⁻¹); (D) fed-batch without solvent and with addition of *t*-BHP (4.38 mmol h⁻¹).

^a An efficiency of 100% indicates that no loss of peroxide by decomposition occurs within experimental error.

tion of *t*-BHP (II), are both influenced by the different reaction modes. The decomposition reaction is second order in the peroxide concentration [32] and therefore strongly dependent on variations in concentration of the peroxide, whereas the selective oxidation is first order in both cyclohexane and peroxide and consequently less dependent on variations in peroxide concentration [32].



The addition of solvent and all reactants at once (Table 2, mode A), results in a fairly high initial reaction rate which rapidly drops. The efficiency is defined as the amount of peroxide used for the selective oxidation of cyclohexane compared to the total amount of peroxide converted. Reaction mode A has a low efficiency. At the end of the reaction, *t*-BHP decomposes

without further oxidation of cyclohexane. As a consequence of the preferential adsorption of polar compounds (Table 1), the cyclohexane concentration near the active sites is low and those of the peroxide, water and acetone high. Therefore, all cyclohexane present in the zeolite is rapidly oxidized. The large excess of peroxide present at the active sites mainly decomposes to *t*-butanol and molecular oxygen resulting in a high initial activity, but a low peroxide efficiency (Table 2, mode A).

To enhance the efficiency, it is essential to keep the concentration of peroxide low in the reaction mixture to suppress the decomposition reaction which is second order in the peroxide [32]. Therefore, the peroxide is added continuously at low rates. A decrease of the rate of addition increases the efficiency, but decreases the reaction rate (Table 2, modes B and C).

The best activity and efficiency is obtained in the absence of solvent (Table 2, mode D), but phase separation occurs during the course of the reaction due to the continuous addition of peroxide. Adsorption measurements (Table 1) show a much higher adsorption of acetone compared to cyclohexane. Therefore, cyclohexane is concentrated in the pores of the zeolite during the beginning period in the absence of solvent and its oxidation is more efficiently (Table 2, mode D). After this initial time period, peroxide, its decomposition product as well as the reaction products accumulate in the reaction mixture and are concentrated in the catalyst, favoring the decomposition of the peroxide at the expense of the selective oxidation of cyclohexane. As phase separation occurs after adding sufficient quantities of *t*-BHP, the reaction procedure requires a more difficult manipulation.

Identical reaction modes are performed with cyclohexanol as substrate and the results are presented in Table 3. Initially, the conversion is highest for the reaction where all peroxide is added at the start (mode A), but the reaction rate drops as the peroxide is decomposed. A fed-batch reactor with slow addition of the peroxide improves the efficiency (mode C), how-

ever decreasing the rate of peroxide addition reduces the conversion (mode B). The most active system is obtained upon performing the reaction fed-batch without solvent (mode D). At the end, all conversions are similar except in the case of reaction mode B, where the conversion is the lowest. Efficiencies in all cases are very high but the absence of solvent (mode D) and the addition of all the peroxide at the start of the reaction (mode A) diminishes them. Rationalization of these results can be done using the same arguments as for cyclohexane oxidation, except that cyclohexanol is polar enough to compete with peroxide, water and acetone as well as with the products for adsorption on the zeolite. The high initial conversion for reaction procedure (A) (Table 3) is the result of the high peroxide concentration at the start of the reaction. All other reaction procedures use a low pumping rate for addition of the peroxide to the reaction mixture. The quantity of oxidant present at short reaction times is too low to give high conversions, explaining the low initial activities for modes B, C and D. Cyclohexanol acts as a suitable solvent for *t*-BHP, avoiding any phase separation (Table 3, mode D). Consequently, the concentration of cyclohexanol near the active sites will be higher than with cyclohexane as reactant and so the activity of the catalyst, especially at the first reaction period. After sufficient reaction time, the other reaction procedures give similar conversions as mode A, except for reaction procedure (B), where the pumping rate of *t*-BHP is too low. When peroxide is added at once (Table 3, mode A), or in the reaction procedure without solvent (Table 3, mode D), *t*-BHP is concentrated in the zeolite, favoring the decomposition. Decomposition of the peroxide also occurs at the end of reaction mode C, in which the peroxide is pumped into the reaction mixture with a rate of 4.38 mmol h^{-1} .

Conditions (C) are preferred, because of the relative high activities and efficiencies and the way of sampling in the homogeneous liquid phase.

3.3.2. Positive effects of zeolite encapsulation on the catalytic performance of the complex

The catalytic performance of FePcY is compared with those of FePc. Identical amounts of FePc are used in the homogeneously catalyzed reaction as in the reaction with the zeolite encapsulated complexes. Two solvents are used for FePc: acetone because it is the same solvent as for the heterogeneous catalyst and dichloromethane in which the solubility of FePc is high and which is commonly used for homogeneously catalyzed reactions with phthalocyanines and porphyrins [1,12]. Using non-incorporated FePc only a minority of the iron-phthalocyanines is dissolved in acetone, whereas complete dissolution occurs in dichloromethane.

Fig. 1 shows the conversion versus time for the oxidation of cyclohexane with FePcY and with FePc in both solvents. The complexes dissolved in dichloromethane are rapidly destroyed. The color of the solution turns from dark green–blue to light yellow in less than 20 min. The active complexes oxidize each other in accordance with literature reports on homogeneous oxidations with phthalocyanines and porphyrins [33–36]. The small increase in conver-

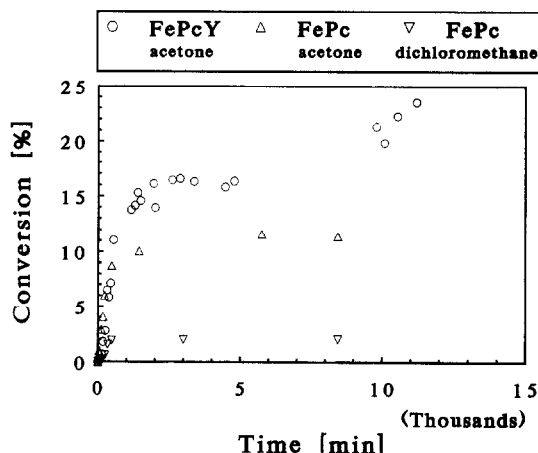


Fig. 1. Oxidation of cyclohexane to cyclohexanol and cyclohexanone as a function of time with 0.5 g FePcY in acetone (○) or 0.025 g FePc catalyst in acetone (△) or in dichloromethane (▽). Conditions: 298 K, 0.1 MPa, 50 ml solvent, 50 mmol substrate and 200 mmol *t*-BHP added to the reaction mixture at a rate of 4.38 mmol h^{-1} .

sion remaining after 20 min is due to reaction with the iron salts in solution. In acetone, the stability and final conversion is considerably higher. Because of the low solubility of FePc in acetone, only a small portion is dissolved and homogeneously catalyzes the oxidation reaction. This portion is also rapidly destroyed, which shifts the FePc solubility equilibrium again and brings some of the remaining solid FePc into solution. Within 10 h, all phthalocyanines were dissolved and consequently oxidatively destroyed as shown by the change in color of the solution. After this period, the activity drops sharply. In contrast, the complexes immobilized in the Y zeolite stay active during the complete reaction period, although some deactivation occurs. The activity of FePcY is as high or even higher than that of the homogeneous catalyst due to the high dispersion. No change in color occurs as the monomolecular dispersion in the supercages inhibits the oxidative destruction. After 10 h reaction the total turnover number (TON) is above 100. The highest TON reported by Herron [13] is only 5.6. In his system the oxidant, iodosobenzene, is disproportionated to iodoxybenzene which causes pore blocking. Since the synthesis method used by Herron [13]

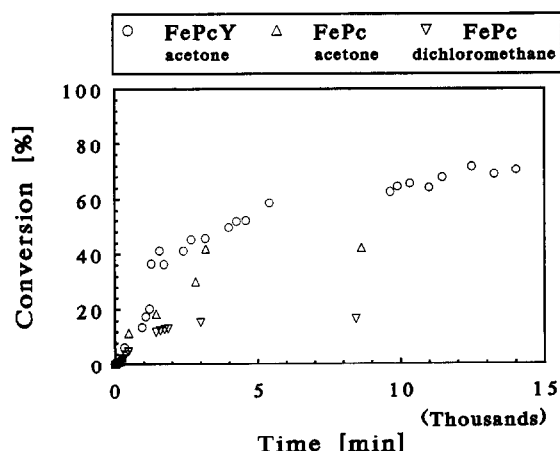


Fig. 2. Oxidation of cyclohexanol to cyclohexanone as a function of time with 0.5 g FePcY in acetone (○) or 0.025 g FePc catalyst in acetone (△) or in dichloromethane (▽). Conditions; 298 K, 0.1 MPa, 50 ml solvent, 50 mmol substrate and 200 mmol *t*-BHP is added to the reaction mixture at a rate of 4.38 mmol h⁻¹.

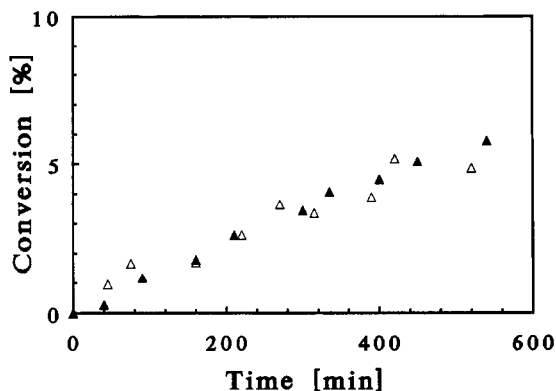


Fig. 3. Oxidation of cyclohexane to cyclohexanol and cyclohexanone as a function of time with 0.5 g fresh (▲) and recycled (△) FePcY catalyst. The recycling occurs by washing the catalyst with acetone and drying for 24 h at 333 K. Conditions are identical to Fig. 1.

leaves free iron ions after reaction in the zeolite, peroxides will be decomposed. Therefore, iodosobenzene was his oxidant of choice.

The conversion versus time curve for the oxidation of cyclohexanol with FePcY and FePc is shown in Fig. 2. Similar observations as in the oxidation of cyclohexane are made. The difference in activity between alkane and alcohol oxidation with FePcY is small within the first few hours but increases owing to a large difference in deactivation rate. The iron-phthalocyanines dissolved in dichloromethane remain active for a few hours and those dissolved in acetone for a day and a half. The longer life-time of the complexes is due to the greater susceptibility of cyclohexanol to be oxidized than cyclohexane.

A simple regeneration, by washing with a polar solvent like acetone and drying (333 K) restores the original activity (Fig. 3 and Fig. 4). It proves that the catalytic entities are not destroyed significantly. FePcY deactivates due to sorption of polar products in the hydrophilic zeolite. Since cyclohexane is less polar than cyclohexanol, the reaction is more sensitive to sorption of polar compounds as shown by a faster deactivation rate.

The efficiency for oxidation of cyclohexane with FePc in dichloromethane is, as could be

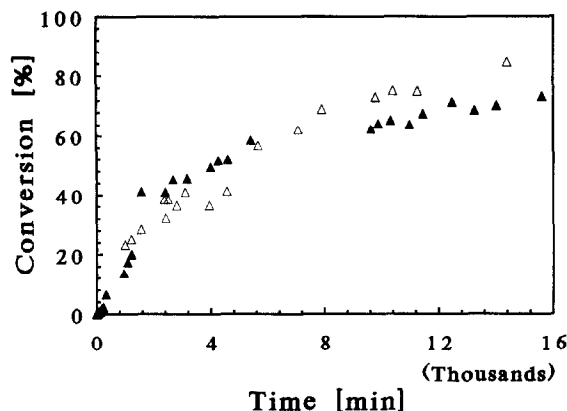


Fig. 4. Oxidation of cyclohexanol to cyclohexanone as a function of time with 0.5 g fresh (\blacktriangle) and recycled (\triangle) FePcY catalyst. The recycling occurs by washing the catalyst with acetone and drying for 24 h at 333 K. Conditions are identical to Fig. 2.

expected from its fast deactivation, very low (< 5%). Cyclohexanol is oxidized by this system with an efficiency below 20%. In acetone, the oxidation occurs more efficiently (Fig. 5), still with a higher efficiency for cyclohexanol than for cyclohexane. The highest efficiencies are obtained on FePcY. For cyclohexane oxidation, they are around 40% initially and decline to a steady state value of 12%. For cyclohexanol the efficiency is initially 100% and declines to a steady state value of 65%. The higher efficiency obtained by the immobilized complexes is due to the absence of iron salts which catalyze Fenton chemistry and decompose the peroxide. The discrepancy in efficiency between cyclohexane and cyclohexanol oxidation is larger for the immobilized complexes than for the homogeneously catalyzed reactions. This cannot solely be the result of differences in sensitivity for oxidation but also sorption effects must play a role. In contrast to cyclohexane, cyclohexanol is polar enough to compete with the other polar compounds for adsorption in the Y zeolite.

The main products in the oxidation of cyclohexane with FePcY are cyclohexanol and cyclohexanone which have a selectivity higher than 95% up to conversions of 25%. The other products (less than 5%) are diketones and diols and

a mixture of both functions. The selectivity for the homogeneous reactions is always below 80% and considerable amounts of cyclohexylhydroperoxide, *t*-butylperoxycyclohexane, *t*-butylcyclohexyl ether and bicyclohexyl are formed. Chlorinated products in dichloromethane and cyclohexylacetone in acetone were also formed. These products were absent for the reactions catalyzed by FePcY indicating the absence of free radical and auto-oxidation reactions with FePcY. The high kinetic isotope effects and its temperature dependence indicate oxidation via an oxo species [23]. In the homogeneously catalyzed reactions, an important contribution exists of oxidation with iron salts which oxidize following a free radical mechanism.

Fig. 6 presents the yield of cyclohexanol and cyclohexanone formed in the oxidation of cyclohexane. It shows initially a rapid formation of cyclohexanol and cyclohexanone. The amount of cyclohexanol goes through a maximum, which is 2.6 mmol after 10 h reaction on FePcY. The maximum is more distinct in the case of the zeolite immobilized complexes. On the other

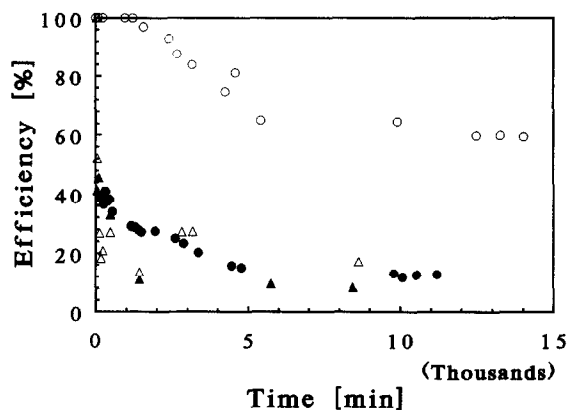


Fig. 5. The peroxide efficiency versus time for the oxidation of cyclohexane and cyclohexanol with FePcY or with FePc. Conditions are identical to Figs. 1 and 2. The efficiency is calculated as the ratio of the amount of peroxide which is used for the selective conversion of the reactant to the total amount of peroxide which is converted. It is based on the assumption that 2 mol *t*-BHP are necessary for the production of 1 mol cyclohexanone from cyclohexane. Symbols: FePcY: cyclohexane (\bullet) and cyclohexanol (\circ); FePc: cyclohexane (\blacktriangle) and cyclohexanol (\triangle).

hand, the amount of cyclohexanone increases during the whole reaction. Obviously, cyclohexanol is a primary product, whereas most of the cyclohexanone is a secondary product. This is not evident, since the ketone could also be formed via direct oxidation of the alkane. The literature contains many examples where high ketone to alcohol ratios are obtained and the complex was not able to oxidize the alcohol [37,38]. The high activity obtained with cyclohexanol as substrate and the selectivity of the alcohol and ketone as a function of the reaction time prove this is not the case here. Therefore, an alternative explanation should be proposed. In terms of polarity, cyclohexane is a rather poor substrate. On the contrary, the alcohol, when formed from cyclohexane, is adsorbed preferentially in the zeolite and further oxidized to the ketone. Secondly, the alcohol function is more susceptible for oxidation. Therefore, the secondary reaction is faster than the primary, explaining the high ketone selectivity in the oxidation of cyclohexane. However, it cannot be excluded that a part of the ketone could be formed by a primary reaction as in GIF chemistry [37,38]. Sorption effects explain also the higher ketone/alcohol ratio obtained with FePcY than with FePc.

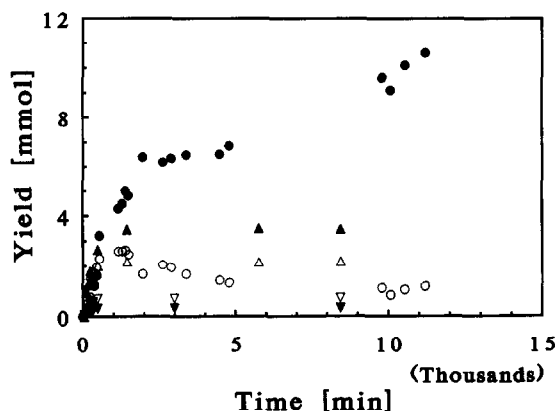


Fig. 6. Cyclohexanol and cyclohexanone produced during the oxidation of cyclohexane with FePcY or with FePc. Conditions are identical to Fig. 1. Symbols: FePcY in acetone: cyclohexanol (○) and cyclohexanone (●); FePc in acetone: cyclohexanol (△) and cyclohexanone (▲); FePc in dichloromethane: cyclohexanol (▽) and cyclohexanone (▼).

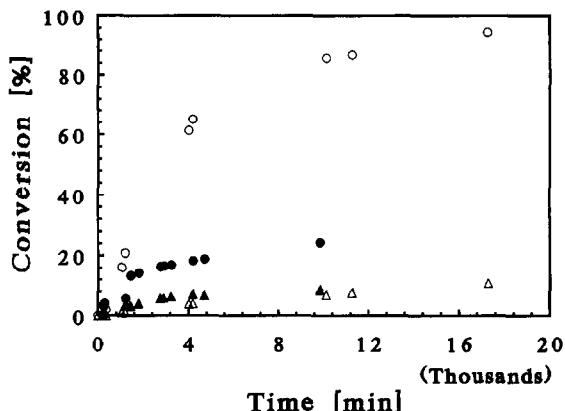


Fig. 7. Competitive oxidation of cyclohexane (25 mmol) and cyclopentanol (25 mmol) with FePcY or with FePc. Conditions: 298 K, 0.1 MPa, 50 ml acetone solvent and 200 mmol *t*-BHP added to the reaction mixture at a rate of 4.38 mmol h⁻¹. FePcY in acetone: cyclopentanol (○) and cyclohexane (△); FePc in acetone: cyclohexanol (●) and cyclohexane (▲).

The competitive oxidation of cyclohexane with cyclopentanol is shown in Fig. 7. Obviously, the conversion for cyclopentanol is much higher than for cyclohexane. The oxidation curve of cyclopentanol under competitive conditions is similar to those obtained for cyclohexanol as pure substrate (Fig. 2): high activity at the start of the reaction and deactivation probably due to depletion of reactants. On the contrary, oxidation of cyclohexane under competitive conditions shows a linear shape with lower activity at the start compared to the oxidation of cyclohexane as a pure substance (Fig. 1). The initial fast conversion of cyclohexane is suppressed in the presence of cyclopentanol. Obviously, without cyclopentanol the concentration of cyclohexane in the interior part of the zeolite is relatively high at the start of the reaction. This results in a high initial rate for cyclohexane oxidation. When cyclopentanol is present in the reaction mixture, it is adsorbed preferentially. Therefore, the concentration of cyclohexane in the interior part of the zeolite is decreased and its oxidation suppressed. The conversion of cyclohexane increases linearly in the competitive oxidation, while a parabolic curve is observed in the separate oxidation. In the competitive oxidation, high amounts of polar compounds, like cyclopent-

tanol, are present at the start of the reaction. The deactivation caused by the addition of supplementary polar compounds then only has a minor effect, resulting in a linear shape of the conversion curve versus time. After the initial period, the rates for both systems are equal, because large amounts of polar compounds are present in the reaction mixture in both cases. The presence of cyclohexane has no influence on the oxidation of cyclopentanol because the latter compound has a favorable polarity. The suppression of the oxidation of cyclohexane on FePcY explains the lower oxidation rate than the one obtained with FePc for cyclohexane oxidation in the competitive experiment. On the contrary, the alcohol is now more rapidly oxidized with FePcY than with FePc (Fig. 7) which is not the case for the non-competitive oxidation (Fig. 2). In the competitive experiment, the amount of cyclopentanol added is half of the amount of alcohol added in the non-competitive reaction. Consequently, the bulk concentration of cyclopentanol is half, but the concentration in the zeolite will not be halved due to the favorable sorption. So reaction rate will not be halved, resulting in higher conversion rates.

4. Conclusions

It is shown that FePcY is a hydrophilic cytochrome P-450 model. The active centre is essentially comparable for both catalysts, but the alteration of the chemical environment of the model catalyst strongly affects the selectivities and the overall yield of the reactions. All results on zeolites can be explained in view of preferential sorption of reagents and products. FePcY prefers hydrophilic substrates and consequently promotes multiple hydrocarbon oxidation, while cytochrome P-450 [39–41] generally releases its products after a single oxidation of an apolar substrate. The activity and stability of the zeolite immobilized complexes is considerably higher than those of homogeneous FePc. FePc, when dissolved, is oxidatively destroyed,

resulting in the formation of iron salts. This reaction is inhibited in the zeolite by the monodispersion of the complex. The present system differs from the one reported by Herron et al. [12] by the new synthesis method which avoids formation of unchelated iron ions and allows the use of peroxides. It gives higher conversions and a stronger dependence of the reaction on sorption effects. To improve the oxidation capability of FePc encaged in zeolites for the oxidation of apolar reactants, the zeolite host should be made more hydrophobic.

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