

Asymmetric cationic methyl pyridyl and pentafluorophenyl porphyrin encapsulated in zeolites: A cytochrome P-450 model

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Abstract

In this work the iron(III)tris(4-*N*-methylpyridyl)-mono(pentafluorophenyl)-porphyrin, [Fe{T(4-*N*-MePy)MFPP}]Cl₄, was impregnated (FeP-NaY_{imp}) and encapsulated (FeP-NaY) in the NaY zeolite and had been used as catalyst in the hydrocarbon oxidation by iodosylbenzene (PhIO) in 1,2-dichloroethane. Cyclohexane, (*Z*)-cyclooctene and adamantane were used as substrate. In the case of cyclohexane, both homogeneous (FePCL₄) and heterogeneous (FeP-NaY_{imp} and FeP-NaY) systems are 100% selective towards the formation of cyclohexanol, indicating that *oxygen rebound mechanism* is operating. The same systems were able to epoxidize (*Z*)-cyclooctene with yields of 92% of *cis*-epoxycyclooctane for heterogeneous catalysts. For the FePCL₄ system the yield of *cis*-epoxycyclooctane obtained was 40%. Probably, this fact is due the low solubility of the FeP in this organic media (1,2-dichloroethane) because when the Cl⁻ counter-ions were exchanged for PF₆⁻ and the solvent used was a mixture consisting of 1,2-dichloroethane/acetonitrile (1:1) the yield of *cis*-epoxycyclooctane increased from 40 to 95%. Hydroxylation of adamantane shows a preferable alkane oxidation at the tertiary C–H bonding as expected for a P-450 model system. The total adamantanol yields were 58, 66 and 81% for [Fe{T(4-*N*-MePy)MFPP}]Cl₄ in solution, [Fe{T(4-*N*-MePy)MFPP}]Cl₄-NaY_{imp} and [Fe{T(4-*N*-MePy)MFPP}]Cl₄-NaY, respectively. Concerning selectivity, the 1-adamantanol (Ad-1-ol)/2-adamantanol (Ad-2-ol) ratio of 19:1 for [Fe{T(4-*N*-MePy)MFPP}]Cl₄ in solution, 19:1 for [Fe{T(4-*N*-MePy)MFPP}]Cl₄-NaY_{imp} and 17:1 for [Fe{T(4-*N*-MePy)MFPP}]Cl₄-NaY were obtained (after statistic correction). These data indicate a free radical activation of the C–H bonds of adamantane, as is expected for a P-450 model. 2-Adamantanone was not obtained in any of the cases.

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Keywords: Iron(III)porphyrin; Iodosylbenzene; Hydrocarbon oxidation; Y zeolite

1. Introduction

The biomimetic systems using synthetic metalloporphyrins (MeP) have offered a great contribution to illustrate the structure of monooxygenases and peroxidases [1]. A possible strategy to turn alkanes more reactive is to find new catalysts able to carry out selective oxidations [2]. Comparative studies of selectivity and stability in the biomimetic oxidations of hydrocarbons in synthetic models and in natural

systems take us to conclude that the selectivity is originated from steric and electronic effects [3–6]. This is the main reason of research on mimicking the protein cavity of natural enzymes. In this sense zeolites are very convenient as an enzymatic model due to the molecular-size channels and pores in three-dimensional network of well defined crystalline structures, conferring shape and size selectivity [7]. Zeolites are formed through a self-assembly mechanism of aluminate and silicate ions around the structure-directing agent [8].

Cationic porphyrins have been extensively studied as template in the synthesis of molecular sieves, such as aluminosilicates, aluminophosphates and gallophosphates. These

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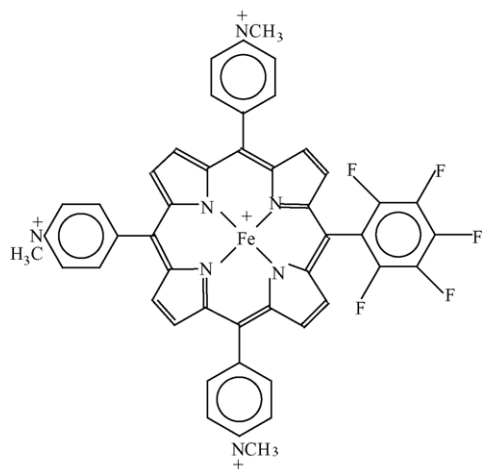


Fig. 1. Iron(III)tris(4-*N*-methylpyridyl)-mono(pentafluorophenyl)porphyrin, represented by: (i) FeP when zeolite encapsulated or impregnated; (ii) and by FePCL₄ or FeP(PF₆)₄ when as a pure solid or in solution.

porphyrins also have the ideal solubility and are stable under the conditions of both molecular and hydrothermal synthesis [9]. One of the methods that attracted a lot of attention consists on the hydrothermal synthesis of faujasite type zeolites in the presence of MeP, referred to as “build-bottle-around-ship” approach [10–12]. This model is proposed as a complete mimic enzymatic of the inorganic matrix [13,14], where the substrate is activated by the porphyrin catalytic centres.

Adamantane is a non-volatile substrate suitable to investigate alkane activation [15]. It has 12 equivalent secondary carbons and four equivalent tertiary carbons and it constitutes a potential probe for regioselectivity, although the interpretation of that selectivity is a matter of continuous controversy [16,17].

In this work it was studied the oxidation of cyclohexane, (*Z*)-cyclooctene and adamantane with iodobenzene (PhIO) catalyzed by the FePX₄ (FeP = iron(III)tris(4-*N*-methylpyridyl)-mono(pentafluorophenyl)-porphyrin), presented in Fig. 1, in solution, impregnated (FeP-NaY_{imp}) and encapsulated in Y zeolite (FeP-NaY). The characterization of the precursor ligand, T(4-*N*-Py)MFPPH₂, was carried out by UV–vis spectroscopy, thin layer chromatography (TLC), FAB MS and ¹H NMR. FePX₄ was characterized by TLC and UV–vis. The FeP-NaY systems were characterized by powder X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectrometry, thermogravimetric and DSC analyses, UV–vis, FT Raman, and IR spectroscopy.

2. Experimental

2.1. Metalloporphyrin synthesis

The synthesis of the T(4-*N*-Py)MPFPH₂, precursor ligand, was carried out according to the method described by

Adler et al. [18]. The compound was isolated by column chromatography on silica gel using dichloromethane/acetone 1:1 as eluent. T(4-*N*-Py)MFPPH₂ obtained was characterized by TLC on silica gel (*R*_f = 0.17 in dichloromethane/acetone 1:1), UV–vis spectroscopy (dichloromethane) λ_{max}, nm (ε, mol⁻¹ dm³ cm⁻¹), 418 (1.7 × 10⁵), 512, 544 (sh), 586, 642 (w). FAB MS (*m/z* 708, calc. av. *m/z* 708) and ¹H NMR (β-pyrrole: δ = 8.87 s (4H), δ = 8.93 d (2H), chemical shift undetermined d (2H), pyridyl: δ = 8.17 d (6H), δ = 9.07 d (2H), N–H pyrrole: δ = –2.91 s (2H)), which confirmed the structure and the purity of the porphyrin. Yield: 6.4%. Iron insertion into T(4-*N*-Py)MFPPH₂ was achieved by heating the free-base porphyrin and FeCl₂·4H₂O at reflux in acetonitrile for 26 h. At the end of the reaction, the solvent was removed under vacuum. The Fe(III)porphyrin was dissolved in water and NaClO₄ was added to the solution, producing a precipitate. The mixture was cooled overnight and the solid Fe(III)porphyrin was isolated by filtration.

The compound was methylated by reaction with large excess (360 equivalents) of CH₃I in *N,N*-dimethylformamide at room temperature under argon [19]. The excess of CH₃I and *N,N*-dimethylformamide was removed under vacuum. The iodide anion was exchanged by chloride using an ion exchange resin Dowex 1 × 2-200 1-chloride (Aldrich). The product gave one spot by TLC on silica using 15% (v/v) methanol in dichloromethane as eluent (*R*_f = 0); UV–vis: (methanol) λ_{max}, nm (ε, mol⁻¹ dm³ cm⁻¹) 350, 418 (1.4 × 10⁴), 580. Yield: 95%.

2.2. FeP-NaY synthesis

Y Zeolite was synthesized in the presence of [Fe{T(4-*N*-MePy)MFPP}]Cl₄ (FeP-NaY), according to the procedure described in references [20,21] for the inclusion of cationic metalloporphyrins inside nanocages of faujasites X and Y during hydrothermal synthesis. The aluminosilicate gel was prepared by stirring colloidal silica (0.46 g), sodium hydroxide (0.62 g), sodium aluminate (0.32 g) and H₂O (8 ml) and finally FePX₄ (0.024 g) was added. The crystallization occurred at 95 °C during 48 h. The complexes adsorbed on the external surface of the zeolite were removed through Soxhlet extractions with distilled water, methanol and 1,2 dichloroethane. The final product was dried at 60 °C for 24 h.

FeP-NaY_{imp} was prepared by impregnation of proportional amounts of FePX₄ (0.1 g) on NaY (1.0 g), followed by filtration of the solid. The sample was submitted to Soxhlet extractions with distilled water, methanol and 1,2-dichloroethane and dried at 60 °C for 24 h.

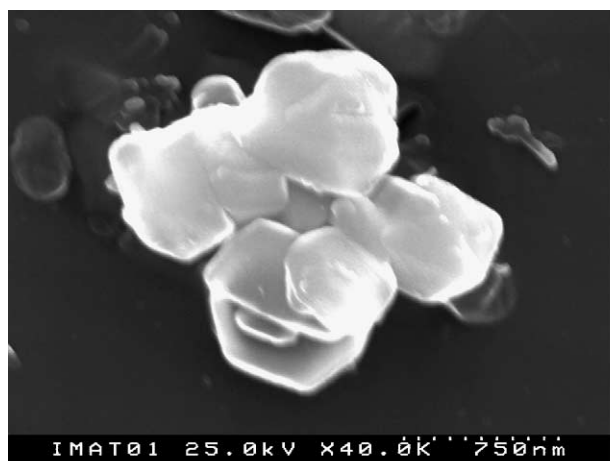
2.3. Catalyst characterization

Powder X-ray diffraction (XRD) of the samples was carried out on a Siemens D 5005 diffractometer using Cu Kα X-radiation. The thermogravimetric (TGA) and DSC curves

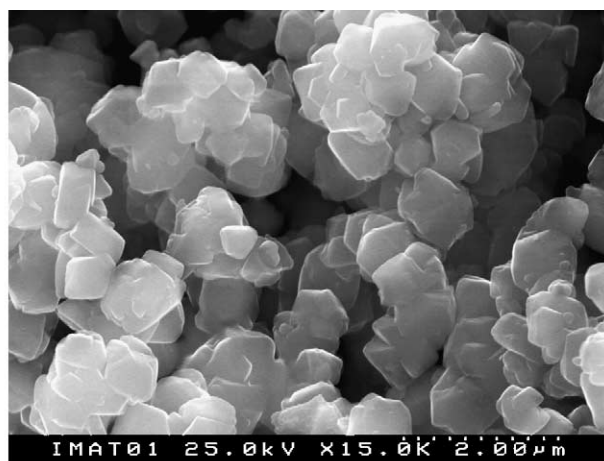
were measured using TA Instruments STD 2690 and DSC Shimadzu analyzers, respectively. The samples were heated at 5°/min until 500 °C under air and kept at this temperature for 10 min. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) were carried out on a Hitachi S-4100 microscope. UV–vis spectroscopy was performed on a HP 8452 A- diode array instrument. The FeP-NaY sample was treated with the concentrated nitric acid to destroy the inorganic framework before recording the UV–vis spectra. No demetallation was observed for the organic macrocycle. The complex loading was estimated using a calibration curve measured with the FePX₄. Raman spectra were recorded on a Bruker RFS 100/S FT Raman spectrometer using 1064 excitation of the Nd/YAG laser. The IR spectra were measured on a Unicam Mattson Mod 7000 FTIR spectrometer using KBr pellets.

2.4. Catalytic reactions

The reactions were carried out in a 8 ml vial sealed with teflon-coated silicone septum. A total of 2.02×10^{-2} mol of 1,2-dichloroethane, the substrate (1.46×10^{-2} mol of cyclohexane or 8.22×10^{-1} mol of (Z)-cyclooctene or 8.90×10^{-4} mol of adamantane) and internal standard (*n*-octanol-7 μl or cyclohexanone-3 μl or benzophenone-30 μl was used in the case of cyclohexane, (Z)-cyclooctene and adamantane oxidation, respectively) were added to the vial containing the catalyst (2.5×10^{-7} mol of FeP) and 5.0×10^{-6} mol PhIO under argon. The mixture was stirred at room temperature (ca. 25 °C). After the reaction the FeP-NaY catalyst was separated from the reaction solution by filtration. The products were analyzed by gas chromatography using a Varian Star GC, Model 3400 CX equipped with a FID detector and a megabore column (30 m × 0.548 mm), and nitrogen as carrier gas. The yield was based on the concentration of the PhIO used. The products were identified by comparison of their retention times with those of authentic samples.



(A)



(B)

Fig. 2. SEM images of NaY (A) and [Fe{T(4-N-MePy)MFPP}]Cl₄ (B).

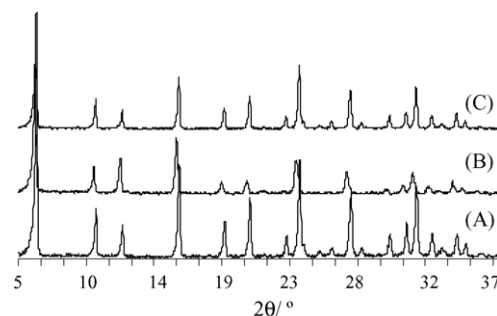


Fig. 3. Powder XRD patterns of NaY (A), [Fe{T(4-N-MePy)MFPP}]Cl₄-NaY (B) and [Fe{T(4-N-MePy)MFPP}]Cl₄-NaY_{imp} (C).

3. Results and discussion

3.1. Catalysts characterization

The SEM image and powder XRD pattern of FeP-NaY presented in Figs. 2 and 3, respectively, are similar to those observed for NaY, indicating that they possess the same morphology and crystalline structures, i.e., the framework around the guest molecule FePX₄ is the faujasite-Y one. The same is observed for FeP-NaY_{imp} (Fig. 3C), suggesting that the solid support is structurally unchanged and the iron(III)porphyrin should be dispersed on the external surface. The Si/Al ratio of the three samples is ca. 1.8, ascertained by EDS.

DSC curves of FeP-NaY and FeP-NaY_{imp} show two small exothermic bands in the temperature range 300–400 °C, which do not appear for zeolite Y, suggesting that they arise from the decomposition of the Fe(III) porphyrin complex (Fig. 4). Indeed, the DSC analysis of FePX₄ gives a broad exothermic band with an onset at ca. 300 °C. The zeolite samples show a broad endothermic band at 50–200 °C, which may be assigned to water loss [22]. The water and organic mass loss of FeP-NaY may be estimated from the TGA curve (for the corresponding temperature intervals) as 23 and 1.1% of the initial mass, respectively. The UV–vis

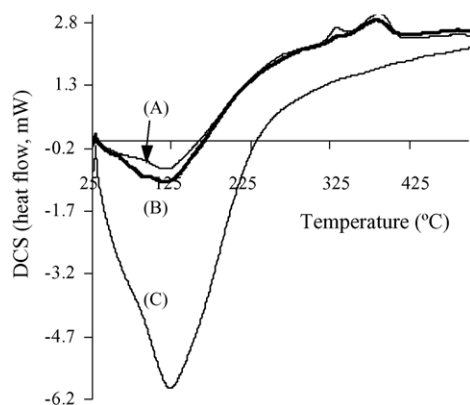


Fig. 4. DSC spectra of $[\text{Fe}\{\text{T}(4\text{-}N\text{-MePy})\text{MFPP}\}]\text{Cl}_4\text{-NaY}_{\text{imp}}$ (A), $[\text{Fe}\{\text{T}(4\text{-}N\text{-MePy})\text{MFPP}\}]\text{Cl}_4\text{-NaY}$ (B) and NaY (C).

spectrum of FeP-NaY is similar to its homogeneous counterpart and from the calibration curve it was possible to estimate a Fe loading of ca. 0.03 wt.%, which is similar to that estimated by atomic absorption, i.e., ca. 0.05 wt.% Fe. These results are in quite good agreement with the organic mass loss, which corresponds to a Fe loading of ca. 0.08 wt.%. Assuming that the sample is only composed of framework silicate and aluminates (with Si/Al ratio of 1.8), sodium cations, water and tetracationic porphyrin, the calculated average unit cell composition is $\text{Na}_{68.2}([\text{Fe}\{\text{T}(4\text{-}N\text{-MePy})\text{MFPP}\}])_{0.2}(\text{AlO}_2)_{69}(\text{SiO}_2)_{123} \cdot 218\text{H}_2\text{O}$. This gives an estimated occupation of approximately one porphyrin per 40 supercages. The complex loading level is similar to that reported in literature for faujasite-Y encapsulated metallotetrakis(*N,N,N*-trimethylanilinium) prepared in a similar fashion [23]. The FT Raman spectra (not shown) of NaY, FeP-NaY and FeP-NaY_{imp} are similar since the zeolite bands mask the spectrum of FeP, present in the low concentration. The FTIR spectrum of FeP-NaY (Fig. 5C) presents some differences in the region 420–820 cm^{-1} , compared to the FeP-NaY_{imp} and NaY (Fig. 5B). This fact probably results from slight changes in the overall structure upon the synthesis of the anionic aluminosilicate framework around the FePX₄

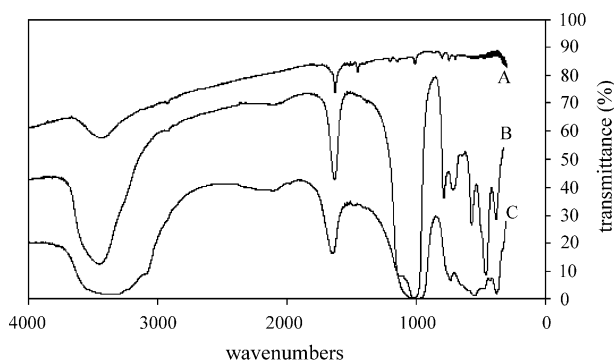


Fig. 5. FTIR spectra of $[\text{Fe}\{\text{T}(4\text{-}N\text{-MePy})\text{MFPP}\}]\text{Cl}_4$ (A), NaY (B), $[\text{Fe}\{\text{T}(4\text{-}N\text{-MePy})\text{MFPP}\}]\text{Cl}_4\text{-NaY}$ (C), NaY and $[\text{Fe}\{\text{T}(4\text{-}N\text{-MePy})\text{MFPP}\}]\text{Cl}_4\text{-NaY}_{\text{imp}}$ traces are the same.

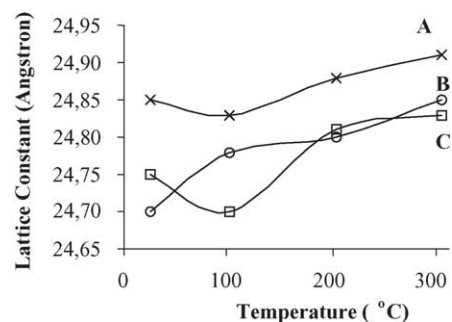


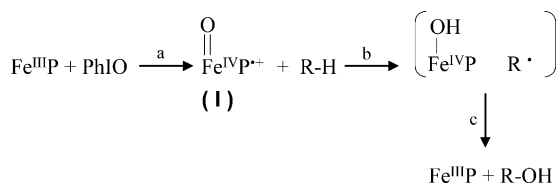
Fig. 6. Influence of temperature on the lattice constant of NaY (C), $[\text{Fe}\{\text{T}(4\text{-}N\text{-MePy})\text{MFPP}\}]\text{Cl}_4\text{-NaY}$ (A), and $[\text{Fe}\{\text{T}(4\text{-}N\text{-MePy})\text{MFPP}\}]\text{Cl}_4\text{-NaY}_{\text{imp}}$ (B).

(Fig. 5 A). The diffraction peaks of these molecular sieves were indexed on cubic unit cells and the Rietveld refined lattice constants (error was always $<0.01 \text{ \AA}$) as a function of temperature are shown in Fig. 6. The influence of the temperature on the inorganic lattice is similar for FeP-NaY and NaY, showing a slight contraction of the framework at 100 °C most likely due the dehydration of the molecular sieves. The fact that the lattice constant of FeP-NaY is higher than that of NaY suggests that the framework of the former is slightly more expanded due to the nanoinclusion of the Fe(III) porphyrin complex. Above 150 °C the lattice constant of the impregnated sample is roughly the same as that of NaY. However, contrary to what is observed for other molecular sieves, the lattice constant of FeP-NaY_{imp} increased upon heating to 100 °C, suggesting that the impregnated porphyrin somehow “disturbed” the framework structure, which is surprising since the complex, is adsorbed on the external surface of the zeolite. It is possible that a significant amount of water (vapor) desorbed upon dehydration becomes trapped inside the aluminosilicate support by the impregnated complexes, which block the pore openings on the external surface, leading to a slight expansion of the framework. It is worthy of mentioning that no significant loss of crystallinity was observed for NaY and FeP-NaY_{imp} upon heating to 400 °C, whereas the FeP-NaY sample showed significant loss of crystallinity upon heating above 300 °C, the temperature at which the porphyrin moiety is decomposed.

3.2. FeP-NaY-catalyzed cyclohexane oxidation

One of the most interesting properties of cytochrome P-450 is its ability to hydroxylate unactivated C–H bonds of alkanes and cycloalkanes. Cytochrome P-450 catalyzed hydroxylation of hydrocarbons is considered to occur by a mechanism involving hydrogen atom abstraction from the substrate (R–H) by the active intermediate $\text{Fe}^{\text{IV}}(\text{O})\text{P}^{\bullet+}$ (I) followed by rapid transfer of the metal-bound hydroxi radical to an intermediate alkyl radical (R \cdot), Scheme 1. This mechanism is so-called *oxygen rebound* [24].

PhIO was chosen as oxygen source because it has been successfully used with P-450 to demonstrate the possibility



Scheme 1.

Table 1

Catalytic activity of FePCL₄, FeP-NaY_{imp}, and Fe-NaY in the oxidation of the cyclohexane by PhIO in 1,2-dichloroethane

Catalyst	Cyclohexanol (%) ^a	Cyclohexanone (%) ^a
FeP(PF ₆) ₄ solution	30 ^b	15 ^b
FePCL ₄ solution	15	–
FeP-NaY _{imp}	25	–
Fe-NaY	38	–

^a Based on PhIO, calculated at 360 min reaction.

^b Solvent is 1,2-dichloroethane:acetonitrile (1:1).

of having a “short” cycle (peroxide shunt) and to support the proposed Fe^{IV}(O)P^{•+} as an active species in P-450 enzymes [25].

In the case of the homogeneous phase oxidation of cyclohexane (Table 1) in the presence of cationic FePCL₄ and FeP(PF₆)₄ in 1,2-dichloroethane and 1,2-dichloroethane/acetonitrile (1:1) respectively, the conversion rate is lower than that observed when the substrate is (Z)-cyclooctene (Table 2), which is expected since, besides the low solubility limitation, cyclohexane is much more inert than cyclooctene. With the homogeneous catalyst FePCL₄ in 1,2-dichloroethane, the yield of the cyclohexanol is 15% and the system is 100% selective towards the formation of alcohol. In this case the hydroxylation occurs, according to Scheme 1 where the Fe^{IV}(O)P^{•+} species abstract hydrogen from the substrate, forming a solvent cage, followed by the rapid transfer of the hydroxyl group from Fe^{IV}(OH)P to the cyclohexil radical (R[•]), the so-called *oxygen rebound mechanism*. However, with the homogeneous catalyst FeP(PF₆)₄, a cyclohexanol yield of 30% and a cyclohexanol/cyclohexanone ratio of 2 is obtained (Table 1), showing that the solvent mixture (1,2-dichloroethane/acetonitrile) can be influencing on the selectivity of this system. Probably the solvent acetonitrile favours the cyclohexil radicals (R[•]) escape from the solvent cage, promoting in this way the absence of selectivity with formation of cyclohexanone besides the alcohol. This fact was observed

Table 2

Catalytic activity of FePCL₄, FeP-NaY_{imp}, and Fe-NaY in the oxidation of the (Z)-cyclooctene by PhIO

Catalyst	<i>cis</i> -Epoxyoctene (%) ^a
FeP(PF ₆) ₄ solution	95 ^b
FePCL ₄ solution	40
FeP-NaY _{imp}	88
Fe-NaY	92

^a Based on PhIO, calculated at 360 min reaction.

^b Solvent is 1,2-dichloroethane:acetonitrile (1:1).

in our group with the system FeTMPyP/PhIO/cyclohexane in acetonitrile (selectivity to cyclohexanol/cyclohexanone ratio of 1) [12].

The heterogeneous systems (impregnated and encapsulated) in 1,2-dichloroethane are also 100% selective towards the formation of cyclohexanol, indicating that *oxygen rebound mechanism* is operating. The yields obtained with these systems were better than for the homogeneous analogues. This is an outstanding performance compared to that previously reported for FeTMPyP, in which case zeolite encapsulation enhanced catalytic activity for cyclohexane oxidation and selectivity to the corresponding alcohol giving a cyclohexanol/cyclohexanone ratio of 10 [12]. In this study the presence of one electron-withdrawing fluorophenyl group was effective to promote selective oxidation.

3.3. Oxidation of (Z)-cyclooctene

The catalytic performance of FePCL₄, FeP-NaY and FeP-NaY_{imp} was studied for the epoxidation of (Z)-cyclooctene with PhIO in order to compare the efficiency of these encapsulated catalysts with each other and with analogous homogeneous systems. This substrate was used because it usually gives a clean conversion into *cis*-epoxycyclooctane and it has been extensively used in earlier metalloporphyrin-catalysed oxidation reactions [12,26,27].

In homogeneous system, the epoxidation of (Z)-cyclooctene by PhIO in the presence of FePCL₄ leads to 40% of *cis*-epoxycyclooctane yield, obtained as the only reaction product (Table 2). The relatively low yield may be explained by the fact that this cationic FeP is not soluble in 1,2-dichloroethane. In order to dissolve the cationic FeP⁴⁺ the Cl⁻ counter-ions were exchanged for hexafluorophosphate PF₆⁻ and the solvent mixture consisting of 1,2-dichloroethane/acetonitrile (1:1) was used. Under these conditions the epoxide yield increased from 40 to 95%. Besides the solubility effect, this anion enhances catalytic activity, most likely by favouring the formation of Fe^{IV}(O)P^{•+} active species. Recently Nam et al. [28] reported for a larger counterion triflate (CF₃SO₃⁻) in the FeP that the complex reacts with PhIO generating the Fe^{IV}(O)P^{•+} active catalytic species and PhI.

FeP-NaY efficiently catalyses the epoxidation of Z-cyclooctene by PhIO in 1,2-dichloroethane, giving rise to *cis*-epoxycyclooctane yields of 92% (Table 2). The encapsulation of FeP renders it more resistant to oxidative self-destruction. The synthesis of zeolite NaY around the cationic water soluble FeP is therefore very important because it seems to produce the heterogeneized encapsulated catalyst, enabling the use of this FeP as catalysts for the oxidation of hydrophobic organic substrates in organic medium.

3.4. Oxidation of adamantane

The catalytic properties of FePCL₄, FeP-NaY and FeP-NaY_{imp}, were further studied for adamantane activation

Table 3
Catalytic activity of FePCL₄, FeP-NaY_{imp}, and Fe-NaY in the oxidation of the adamantane by PhIO

Catalyst	Ad-1-ol (%) ^a	Ad-2-ol (%) ^a	Total yield (%)	Ad-1ol/Ad-2-ol ^b
FePCL ₄ solution	50	8	58	19
FeP-NaY _{imp}	58	9	67	19
FeP-NaY	69	12	81	17

^a Based on PhIO, calculated at 360 min reaction.

^b Statistically corrected.

and the only reaction products observed were 1- adamantanol (Ad-1-ol) and 2- adamantanol (Ad-2-ol) (2- adamantanone is not obtained in any of these cases), indicating that in all cases *the oxygen rebound mechanism* had been favoured. Control experiments showed that PhIO without catalyst or NaY zeolite were inactive, under the operating conditions, indicating that the catalytically active species are formed from FeP. All catalysts used led to relatively high total alcohol yields (based on PhIO), which increased in the order: FePCL₄ in solution (58%) < FeP-NaY_{imp} (67%) < FeP-NaY (81%). These results may be due to the increased catalyst stability upon immobilization on the zeolite matrix and the high dispersion of FeP compared of bulk FeP.

All catalysts possess regioselectivity towards the hydroxylation of adamantane at the C2 position (Table 3) and the dependence of products selectivity on reaction time is shown in Fig. 7. FePCL₄ and FeP-NaY_{imp} gave a Ad-1-ol/Ad-2-ol molar ratio of 19:1 (calculated at 360 min), whereas FePCL₄-NaY, gave a Ad-1-ol/Ad-2-ol ratio of 17:1 (after statistical correction), showing a preferable alkane oxidation at the tertiary C–H bond. These results indicate a free radical activation of the C–H bonds of adamantane, in all of the systems, as is expected for a P-450 model [25].

All of the catalysts presented similar kinetic profiles. The product yield increases with time until 5 h of reaction, after which it remains unchanged until 24 h.

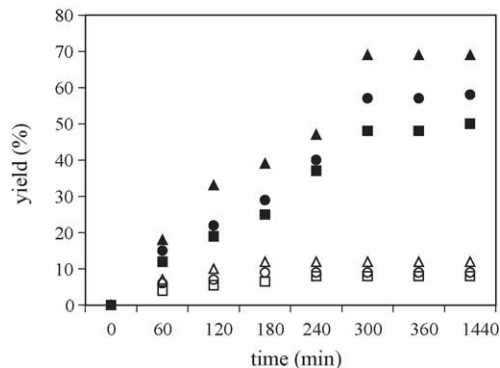


Fig. 7. Build-up of Ad-1-ol (solid symbols) and Ad-2-ol (open symbols) in the adamantane oxidation catalysed by [Fe{T(4-N-MePy)MFPP}]Cl₄ (□), [Fe{T(4-N-MePy)MFPP}]Cl₄-NaY (Δ) and [Fe{T(4-N-MePy)MFPP}]Cl₄-NaY_{imp} (○).

4. Conclusions

Based on the characterization of the catalysts using several techniques, it may be suggested that the preparation of FeP-NaY led to the successful inclusion of the iron(III)porphyrin inside the aluminosilicate framework. The approach adopted herein for the obtention of zeolite encapsulated and impregnated ironporphyrins leads to the clean syntheses of the desired catalysts, avoiding the formation of unchelated iron ions. In the oxidation of cyclohexane, both bulk FePCL₄ and supported FeP-NaY_{imp} and FeP-NaY catalytic systems are 100% selective towards the formation of cyclohexanol, indicating that *oxygen rebound mechanism* is operating. The same systems were able to epoxide (*Z*)-cyclooctene with yields of 92% of *cis*-epoxycyclooctane for encapsulated catalysts. For the FePCL₄ system the yield of *cis*-epoxycyclooctane obtained was 40%. Probably, this fact is due the low solubility of the FeP in this organic media (1,2-dichloroethane). All of the systems studied presented relatively high catalytic activity for adamantane oxidation. The regioselectivity was observed in all of the cases since 2- adamantanone (Ad-2-one) was not obtained and 1-adamantanol (Ad-1-ol) was always the main product. Therefore, the zeolite NaY is a good mimic of cytochrome P-450 enzyme protein cavity, showed by the preference of the adamantane hydroxylation at the tertiary C–H bond, protecting the iron(III)porphyrin from degradation. The encapsulation of FePCL₄ in NaY zeolite minimizes self-destruction of the porphyrin. The activity of the FeP-NaY and FeP-NaY_{imp} is considerably higher than its homogeneous counterpart FePCL₄.

Acknowledgements

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