

Oxidation of pinane to 2-pinane hydroperoxide over encaged metal phthalocyanines in Y zeolites. Mechanism and kinetic modelling

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Abstract

The influence of the oxygen donor (*t*-butyl hydroperoxide [*t*-BHP], O₂, H₂O₂) and the central metal (Cu, Co, Fe, Mn), on the activity and selectivity of metallophthalocyanines when free or encaged in NaY, for the oxidation of *cis*-pinane, is reported. The effect of encapsulation enhances catalyst stability and influences its activity and selectivity. Encaged complexes yield mainly 2-pinane hydroperoxide and insignificant amounts of 2-pinanol, while with their homogeneous counterparts, selectivities to 2-pinanol are higher. The ratio of 2-pinane hydroperoxide/2-pinanol depends on the amount of the complex, indicating that 2-pinane hydroperoxide is also in this last case, the primary oxidation product. With the purpose of checking the effect of the concentration of the oxidant agent on selectivity, oxidation experiments were carried out with slow addition of *t*-BHP, under semibatch conditions. A chain reaction mechanism initiated by *t*-BHP decomposition is proposed and a kinetic model was built for the semibatch reactor assuming internal mass transfer limitations concerning pinane. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The oxidation of pinane **1** to 2-pinane hydroperoxide **2** is one step of the so-called “ α -pinene route” for linalool that has been used as a feedstock for the manufacture of vitamin E and flowery-fresh-based fragrances such as nerol and geraniol [1,2]. Linalool can be obtained by reducing the hydroperoxide to 2-pinanol **5** fol-

lowed by subsequent pyrolysis of this alcohol [1–3].

The catalytic properties of transition metal complexes encapsulated in zeolite cavities for oxidation catalysis have become of considerable interest. Encaged transition metal complexes combine the advantages of homo and hetero catalytic systems. Zeolites can replace the protein mantle of natural enzymes and influence the reactivity in the same way as enzymes do by exerting steric constraints on the environment of the active transition metal complex making them differ from the solution species [4–8]. The atoms

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within the cavities of the inorganic matrix create an electric field that imposes steric constraints on the encapsulated complex, thus modifying properties of the latter, like stability, activity and selectivity [9]. The selectivity is influenced by size constraints in the zeolite cages. Encapsulation will enhance the activity and lifetime of the catalyst since the zeolite framework, like an enfolding protein, suppresses degradation pathways such as dimerization and autoxidation [6–16].

Encapsulated metallophthalocyanines in the supercages of Y zeolite have been proposed as enzyme mimics [11–17]. In such a host–guest system, the guest is retained by spatial restrictions and the access to the metal active site is limited by sterical restrictions imposed by the surrounding aluminosilicate framework of the zeolite. Such catalysts combine characteristics of the support, like pore diameter, cavity size, electrostatic potential, with the electronic and stereochemical properties of the complex [14].

In a previous work, we reported the oxidation of **1** with *t*-butyl hydroperoxide (*t*-BHP) in the presence of iron and cobalt phthalocyanines encapsulated in NaY zeolites [18]. The main reaction product was **2**, achieving high selectivities (~ 90%) at high conversions (~ 80%). Thermal decomposition of **2** into substituted cyclobutanes was only observed in low extent. In contrast to the reaction in homogeneous phase, products of oxidation on C3 and C4 were not observed. However, those experiments were carried out with a large excess of *t*-BHP, what is expectable to lead to an excessive peroxide decomposition [24–26].

According to what has been described in previous works on the oxidation of cyclohexane (Ref. [24] and references therein), a strong influence of the concentration of *t*-BHP on selectivity should be expectable. In the present work, we report the results of the oxidation of **1** by *t*-BHP in the presence of metallophthalocyanines, in a semibatch reactor at 20°C, in acetone/*t*-butanol. When the reaction is started, there is no *t*-BHP in the reaction mixture, being

that reagent fed continuously to the reactor at a low flow rate (0.1 ml/h). Therefore, *t*-BHP concentration is slowly increased during the course of the reaction. A mechanism is proposed and a kinetic model is developed for the semibatch reactor.

The influence of the oxygen donor and the central metal on the activity and selectivity of metallophthalocyanines, when free or engaged in NaY, are also reported.

2. Experimental

2.1. Catalyst synthesis

Encapsulated metallophthalocyanine catalysts ($M\text{PcNaY}$; $\{M = \text{Cu, Co, Mn}\}$) were prepared by ion exchanging NaY (Aldrich) zeolite with the corresponding transition metal ions prior to encapsulation. This procedure was carried out by suspending NaY in a 0.02 M solution of the respective metal salt and stirring at 363 K for 24 h. The mixture was filtered and the residue was washed with distilled water.

In situ synthesis of metallophthalocyanines, in the supercages of zeolite NaY was carried out by heating ion-exchanged zeolites with molten, organic precursor, 1,2-dicyanobenzene (8 DCB:1 metal ion) at 523 K for 4 h.

Undesired material was removed by extended soxhlet extractions with acetone, dimethylformamide and again with acetone. Finally, all catalyst samples were ion-exchanged with an aqueous NaCl solution.

FePcNaY was synthesised according to a procedure described in Ref. [18].

Standard Mn(II)Pc, Fe(II)Pc, Co(II)Pc and Cu(II)Pc complexes were purchased from Aldrich.

2.2. Catalyst characterisation

UV spectra used for a semi-quantitative determination of the amount of intracrystalline

phthalocyanine complexes were taken on a Perkin Elmer UV–visible spectrophotometer. A calibration curve was obtained by dissolving known amounts of a metal complex in concentrated sulphuric acid. Zeolite was added to take into account matrix effects. Surface area and pore volume measurements were performed on a Micromeritics ASAP 2010 by adsorption of nitrogen gas at liquid nitrogen temperature. X-ray powder diffraction of the zeolites was used to ensure good crystallinity after the exchange and encapsulation procedures.

2.3. Catalytic experiments

cis-Pinane 97–98% pure was obtained from α -pinene by reduction with diimide [19]. Oxidation reactions of pinane were carried out at 20°C and atmospheric pressure. Semibatch experiments were performed by loading a three-neck round flask equipped with a mechanical stirrer, with pinane, acetone/*t*-butanol (9:1 volume ratio) as solvent and the catalyst. A *t*-BHP water solution 70% (w/w–Aldrich) was loaded in a syringe infusion pump. The reaction was started after temperature stabilisation, by starting the pump, using a flow rate of 0.1 ml/h. In a typical experiment, the reactor was loaded with 460 mg of pinane, 7 ml of solvent and 36 mg of encapsulated zeolite. A total amount of 4 ml of *t*-BHP was loaded in the syringe pump.

Batch experiments were carried out loading pinane, solvent, catalyst and the oxygen donor (*t*-BHP, H₂O₂ or O₂) in a molar ratio of 8:1 to pinane, all together in the three-neck flask. In the experiments carried out with the free complexes, the amount of catalyst used was that corresponding to the amount engaged in the encapsulated catalysts.

Samples were treated with aqueous sodium sulphite and analysed by GC and GCMS on a 30 m × 0.25 mm DB-1 column from J&W, before and after the reductive treatment.

The decomposition of *t*-BHP by *M*PcNaY catalysts was followed by iodometric titration.

3. Results and discussion

3.1. Catalyst characterisation

The amount of intracrystalline complex present in the different catalyst samples was determined by UV spectroscopy of the sample dissolved in concentrated sulphuric acid (Table 1).

The surface areas and the total microporous volumes were measured after encapsulation of the complex in the zeolite supercages (Table 2). Langmuir surface areas and total pore volumes decrease upon encapsulation.

X-ray diffraction patterns of the catalyst samples showed no variation after the synthesis and purification procedures.

3.2. Oxidation experiments

The main product of oxidation of **1** with encapsulated metallophthalocyanine Y zeolites, at room temperature and atmospheric pressure, is **2**. Products of the oxidation of pinane on C3 and C4, like pinocampheol **3**, verbanol **4** and the corresponding ketones, as well as **5** were mainly formed in the homogeneous phase oxidation with FePc and MnPc (Scheme 1).

Encapsulation influences the catalyst's activity and selectivity (Figs. 1 and 2). The highest selectivity to **2** was observed with encapsulated copper (80%) at 90% conversion (Fig. 1A). Encaged complexes yield insignificant amounts of **5**, being a maximum selectivity of 6% achieved for CuPcNaY (Fig. 1A). With their homogeneous counterparts, selectivities to **5** are

Table 1
UV spectrophotometry analysis

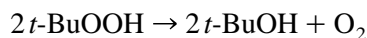
	mmol <i>M</i> Pc/g zeolite	<i>M</i> Pc/ zeolite (% wt)	Percentage occupied supercages
CuPcNaY	4.47×10^{-2}	2.57	7.3
CoPcNaY	4.67×10^{-2}	2.67	7.4
FePcNaY	4.79×10^{-2}	2.72	7.9
MnPcNaY	4.63×10^{-2}	2.63	7.6

Table 2
Surface analysis

Catalyst sample	Langmuir surface area (m ² /g)	Total micropore volume (cm ³ /g)
NaY	984	0.392
CuPcNaY	685	0.329
CoPcNaY	647	0.323
FePcNaY	612	0.265
MnPcNaY	599	0.288

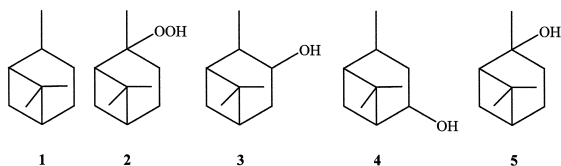
higher. In particular, for FePc, selectivity to **5** can be as high as 19% and no **2** is formed (Fig. 2C).

The formation of **2** may suggest that molecular oxygen is involved in the reaction. The latter is generated during *t*-BHP decomposition according to the scheme [20,21]:



Transition metal ions are well known to catalyse the decomposition of organic peroxides [21–23]. It has been reported that metalloporphyrin and metallophthalocyanine complexes that are active for the selective low-temperature oxidations of alkanes are also highly efficient catalysts for the selective decomposition of alkylhydroperoxides to alcohols [13,23,24,27]. Other authors agree that zeolite Y is quite hydrophilic so it favours sorption of polar compounds, such as solvent, water, oxidation products and peroxide [24,25]. The high sorption of peroxide in the zeolite induces excessive peroxide decomposition [24,26].

According to Parton et al. [24], the decomposition of *t*-BHP is second order in the peroxide concentration and therefore strongly dependent on variations in concentration of the peroxide. In order to enhance the efficiency of the cyclo-



Scheme 1.

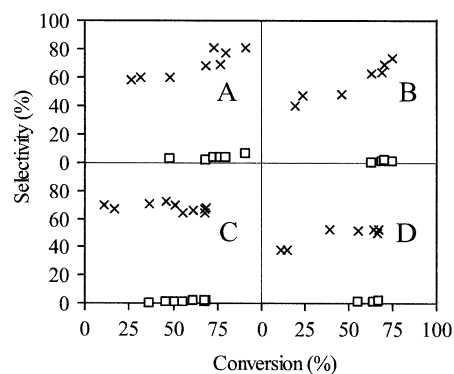


Fig. 1. Selectivity to 2-pinane hydroperoxide (X) and 2-pinanol (□) for the oxidation reactions carried out with encapsulated phthalocyanines. (A) CuPcNaY; (B) CoPcNaY; (C) FePcNaY; (D) MnPcNaY.

hexane oxidation, those authors fed the *t*-BHP at slow rates. To check the effect of *t*-BHP concentration on the oxidation of **1**, we performed also semibatch experiments, slowly feeding the peroxide (Fig. 3). In these experiments, there was no oxidant inside the reactor at the reaction starting time. *t*-BHP (70% w/w) was then slowly added at a flow rate of 0.1 ml/h. Under these conditions, the main product continues to be **2** and selectivity to **5** is less than 1%. No significant changes in product distribution are observed when the whole amount of oxidant is added in one single initial stage or gradually added during the course of the reaction. Selectivity to **2** is higher in semibatch

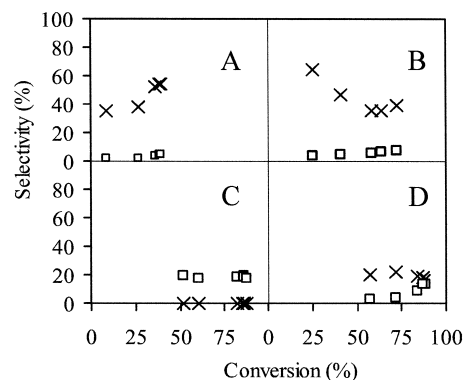


Fig. 2. Selectivity to 2-pinane hydroperoxide (X) and 2-pinanol (□) for the oxidation reactions carried out with free phthalocyanines. (A) CuPc; (B) CoPc; (C) FePc; (D) MnPc.

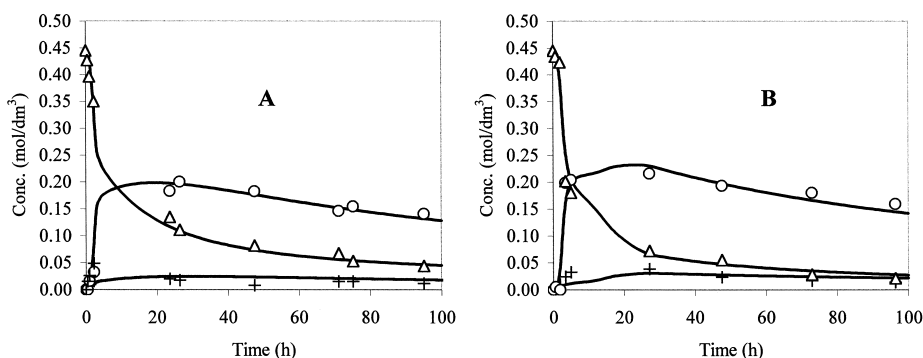


Fig. 3. Model fitting to data points obtained with the semibatch reactor. (A) FePcNaY; (B) CuPcNaY. Δ : Pinane; \circ : 2-pinane hydroperoxide; $+$: other products.

conditions than in batch conditions (more than 95% at $\sim 75\%$ conversion for FePcNaY). This improvement in selectivity observed in semibatch conditions is likely to be due to a more favourable lipophilic/hydrophilic balance in the reaction medium within the zeolite pore system. In fact, in batch conditions, a huge amount of water and *t*-BHP is added to the reaction mixture. Due to the hydrophilicity of the zeolite surface, the reaction medium within the zeolite supercages is most probably rich in those substances. Therefore, in this case, diffusion of **1** to the zeolite pore system is more difficult and the oxidation reaction takes place, to some extent, in the bulk. On the contrary, in semibatch conditions, diffusion of **1** to the zeolite pores is easier. The reaction takes place to a much higher extent in the supercages; therefore, selectivity to **2** is higher.

According to what has been reported by Parton et al. [7,11,15] for cyclohexane oxidation with *t*-BHP using encapsulated *M*Pc complexes, direct formation of significant amounts of **5** should be observed which is not the case with encapsulated *M*Pc complexes. However, with free *M*Pc complexes, **5** is formed, which can even be the main product in the case of free FePc. When the amount of free FePc complex is reduced by a factor of 10, selectivity to **2** increases (from 0% to 30% in the case of FePc). These results suggest that the oxygen rebound mechanism proposed by Parton et al. [7,11,15,24] for cyclohexane oxidation is not valid for

pinane oxidation in the presence of free or encapsulated *M*Pc complexes. Instead, **2** is in both cases, the primary oxidation product. In homogeneous phase, **2** easily reaches the central metal of the complexes being reduced to **5**, what explains the highest selectivity to this alcohol in those conditions.

The initial catalytic activity for pinane oxidation of free and encapsulated complexes exhibits opposite behaviours: while with encapsulated complexes the catalyst activity increases in the order Mn(II) < Fe(II) < Co(II) < Cu(II), with the free complexes, the catalyst activity decreases in the same order Mn(II) > Fe(II) > Co(II) > Cu(II). This dependence of activity on the central metal is a strong indication that metal complexes play an important role in the reaction mechanism. Since pinane hydroperoxide is the primary product in the presence of free or encapsulated *M*Pc complexes, the role of the metal complexes is most probably the metal-catalysed homolytic decomposition of *t*-BHP. This decomposition proceeds via reactions generating chain initiating radicals for which relative reaction rates have been roughly correlated with the redox potential of the $M^{(n+1)}/M^{n+}$ couple [28]. However, to our knowledge, the redox potentials of *M*Pc complexes in organic solvents are unknown. It seems somehow vague to relate the activity of these complexes to known standard redox potentials of the corresponding metal ions (determined in aqueous solution) since the ligands and the sol-

vents significantly influence the electrochemical behaviour of the complexes [29–32]. Moreover, the superstructure of the molecular sieve can modify the redox potential of the metal complex by imposing an unusual (high energy) geometry at the central metal atom [21].

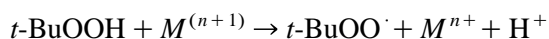
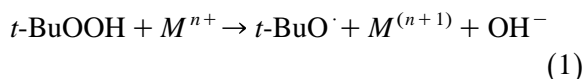
Anyway, the observed differences in the activity order for pinane oxidation between free and encaged complexes have more to do with the protection given to the complex molecules by the zeolite structure, than any other factors. In fact, although CoPc and CuPc show the lowest activities towards pinane conversion, a rapid changing in the colour of the respective reaction mixtures is observed, clearly indicating destruction of the complexes.

From what has been said above, we may assume the following hypothesis for the pinane oxidation in the presence of free or encaged MPc complexes:

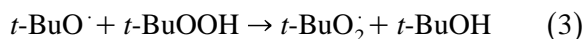
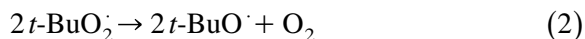
- (i) the primary product of pinane oxidation by *t*-BHP in the presence of free or encaged metal phthalocyanines is 2-pinane hydroperoxide;
- (ii) the role played by the MPc complexes consists the metal-catalysed homolytic decomposition of *t*-BHP, via reactions generating chain initiating radicals;
- (iii) due to steric hindrances, pinane molecules cannot approach the metal active site of the encaged complex, that is, they only react with the generated radicals in supercages in the vicinity of that occupied by metallophthalocyanines;
- (iv) in homogeneous phase, with free complexes, 2-pinane hydroperoxide is also decomposed, leading to 2-pinanol. This decomposition occurs more or less extensively, depending on the amount of complex present;
- (v) in heterogeneous phase, with the encaged complexes, and also due to steric hindrances, 2-pinane hydroperoxide molecules cannot approach the metal centre, what explains the high selectivity observed.

Based on the above hypothesis, the following mechanism is proposed:

The main role of the metal phthalocyanines is the decomposition of *t*-BHP via steps (1) and (2), in agreement with what has being proposed for the metal-catalysed decomposition of alkylhydroperoxides [28]:



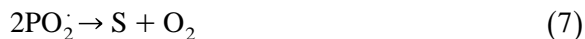
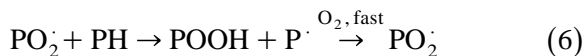
These reactions can be followed by the radical chain decomposition of the hydroperoxide according to the following steps [28]:



It is assumed that the termination step occurs exclusively by the self-reaction of two alkoxi radicals according to reaction:



Similar to what has been proposed by previous models for the autoxidation of saturated hydrocarbons, we consider the following reactions for pinane chain reaction autoxidation, assuming fast reaction of hydrocarbon radicals with molecular oxygen [32–35]:



where PH and POOH stand for pinane and pinane hydroperoxide, respectively, and S lumps several minor products resulting from the cyclohexane ring opening.

Assuming this mechanistic proposal, a kinetic model was built for the reaction carried out in heterogeneous phase, under semibatch conditions. The following simplifying assumptions were made:

All the reactions take place inside the zeolite supercages.

Since the zeolite surface has a hydrophilic character, mass transfer limitations are assumed only for pinane.

During the course of the reaction, the nature of the reaction mixture changes, not only due to the continuous addition of *t*-BHP and water, but also due to the formation of pinane hydroperoxide. Because of the hydrophilic character of the zeolite surface, it is expected that the reaction mixture inside the zeolite supercages becomes increasingly richer in the more polar components, namely hydroperoxides and water, what means that the transport of pinane into the zeolite becomes more and more difficult. Therefore, it is reasonable to assume that the value of pinane diffusivity decreases exponentially with the amount of *t*-BHP solution added as well as the amount of pinane hydroperoxide formed. Denoting by \mathcal{D}_{e0} the initial pinane diffusivity in the catalyst particle, instantaneous diffusivity could be given by:

$$\mathcal{D}_e = \frac{\mathcal{D}_{e0}}{1 + e^{\alpha v_0 t} + e^{\beta[\text{POOH}]}}$$

where t is the time, v_0 is the feed volumetric flow rate and α and β are the adjustable parameters.

From the above mechanism, we get the elementary reaction rates:

$$r_1 = k_1[t\text{-BuOOH}],$$

$$r_2 = k_2[t\text{-BuOO}\cdot]^2,$$

$$r_3 = k_3[t\text{-BuOOH}][t\text{-BuO}\cdot],$$

$$r_4 = k_4[t\text{-BuO}\cdot]^2,$$

$$r_5 = k_5[\text{PH}][t\text{-BuO}\cdot],$$

$$r_6 = k_6[\text{PH}][\text{POO}\cdot],$$

$$r_7 = k_7[\text{POO}\cdot]^2$$

As we are assuming diffusional limitations for pinane, a mole balance to the catalyst particle assuming spherical shape, is made:

$$\frac{d\mathcal{F}_{\text{PH}}}{dx} = \left(-r_{\text{PH}} \rho_p - \frac{2}{x} \mathcal{F}_{\text{PH}} \right)$$

where \mathcal{F}_{PH} is the molar flux of pinane, ρ_p is the density of the catalyst particle and r_{PH} is the rate of formation of pinane, both at the linear dimension x measured along the catalyst particle radius.

The molar flux of pinane is given by Fick's law:

$$\mathcal{F}_{\text{PH}} = -\mathcal{D}_e \frac{d[\text{PH}]}{dx}$$

Taking into account the mechanistic proposal, the rates of formation of pinane, pinane hydroperoxide, *t*-BuO \cdot and POO \cdot are given by:

$$r_{\text{PH}} = -r_5 - r_6,$$

$$r_{\text{POOH}} = r_6,$$

$$r_{t\text{-BuO}\cdot} = r_1 + 2r_2 - r_3 - 2r_4 - r_5,$$

$$r_{\text{POO}\cdot} = r_5 - 2r_7$$

The above equations are integrated assuming the following boundary conditions: $[\text{PH}] = [\text{PH}]_{\text{bulk}}$ at $x = R$, where R is the radius of the catalyst particle and $[\text{PH}]_{\text{bulk}}$ is the bulk concentration of pinane; $4\pi R^2 \cdot \mathcal{F}_{\text{PH}|x=R} = -\mathcal{R}_{\text{PHobs}} \rho_p (4/3)\pi R^3$, where $\mathcal{F}_{\text{PH}|x=R}$ is the molar flux of pinane on the external surface of the catalyst particle, $\mathcal{R}_{\text{PHobs}}$ is the experimental reaction rate for pinane formation, which is easily calculated from the slope of the experimental concentration profile for each value of time, and ρ_p is the catalyst particle density.

The overall reaction rates for the formation of pinane, pinane hydroperoxide, *t*-BuO \cdot and POO \cdot , \mathcal{R}_{PH} , $\mathcal{R}_{\text{POOH}}$, $\mathcal{R}_{t\text{-BuO}\cdot}$ and $\mathcal{R}_{\text{POO}\cdot}$, are obtained by integrating the local rates r_{PH} , r_{POOH} , $r_{t\text{-BuO}\cdot}$ and $r_{\text{POO}\cdot}$, all over the catalyst particle:

$$\mathcal{R}_i = \frac{\int_0^R r_i \rho_p 4\pi x^2 dx}{\int_0^R \rho_p 4\pi x^2 dx}$$

The overall reaction rates for the remaining species are directly derived from the proposed mechanism:

$$\mathcal{R}_{t\text{-BuOOH}} = -2r_1 - r_3,$$

$$\mathcal{R}_{t\text{-BuOO}\cdot} = r_1 - 2r_2 + r_3,$$

$$\mathcal{R}_S = r_7$$

Applying a mole balance to the semibatch reactor for all the chemical species, a final set of differential equations can be written:

$$\frac{d[\text{PH}]}{dt} = (-[\text{PH}])\frac{v_0}{V} + \mathcal{R}_{\text{PH}}\left(\frac{W}{V}\right)$$

$$\begin{aligned} \frac{d[t\text{-BuOOH}]}{dt} &= ([t\text{-BuOOH}]_0 - [t\text{-BuOOH}])\frac{v_0}{V} \\ &+ \mathcal{R}_{t\text{-BuOOH}}\left(\frac{W}{V}\right) \end{aligned}$$

$$\frac{d[\text{POOH}]}{dt} = (-[\text{POOH}])\frac{v_0}{V} + \mathcal{R}_{\text{POOH}}\left(\frac{W}{V}\right)$$

$$\frac{d[t\text{-BuO}\cdot]}{dt} = (-[t\text{-BuO}\cdot])\frac{v_0}{V} + \mathcal{R}_{t\text{-BuO}\cdot}\left(\frac{W}{V}\right)$$

$$\begin{aligned} \frac{d[t\text{-BuOO}\cdot]}{dt} &= (-[t\text{-BuOO}\cdot])\frac{v_0}{V} + \mathcal{R}_{t\text{-BuOO}\cdot}\left(\frac{W}{V}\right) \end{aligned}$$

$$\frac{d[\text{POO}\cdot]}{dt} = (-[\text{POO}\cdot])\frac{v_0}{V} + \mathcal{R}_{\text{POO}\cdot}\left(\frac{W}{V}\right)$$

$$\frac{d[\text{S}]}{dt} = (-[\text{S}])\frac{v_0}{V} + \mathcal{R}_S\left(\frac{W}{V}\right)$$

where $[t\text{-BuOOH}]_0$ is the concentration of *t*-BHP in the feed and V is the instantaneous volume of the reaction mixture. Making V_0 the initial volume of the reaction mixture:

$$V = V_0 + v_0 t$$

Model equations were numerically integrated with a simple computer program [36]. Fig. 3A

and B shows the model fitting to data points for the semibatch experiments carried out in the presence of FePcNaY and CuPcNaY. Models assuming pseudo-homogeneous reaction, only taking into account the chain radical mechanism, or assuming a constant diffusivity for pinane, were also tested. In all those cases, the predicted kinetic curves fitted data points only in an initial period of about 5 h, exhibiting the initial inductive period that is particularly noticeable in the case of the copper catalyst, but failed in fitting data points above 20 h of reaction. To conciliate the high initial reaction rate observed in that initial period of 5 h with the low rate observed above 20 h, internal-diffusion-limitations concerning pinane transport into the catalyst particle and a very fast changing of pinane diffusivity, were assumed. Finally, it should be emphasised that the reasonable good fitting achieved has no other meaning that the assumptions made are valid and reasonable.

Catalytic activity also depends on the oxygen donor, having been observed the order $t\text{-BHP} \gg \text{O}_2 > \text{H}_2\text{O}_2$. The much lower activity observed when molecular oxygen is used as oxygen donor is easily explained by the low solubility of O_2 in the reaction mixture. However, when H_2O_2 is the oxidant, due to the high hydrophilicity of Y zeolite, its porous structure adsorbs preferentially the abundant oxidant and water molecules. Therefore, the access of **1** to the inner structure of the zeolite is inhibited. Consequently, pinane conversion is very low when the oxidant is aqueous H_2O_2 . In turn, *t*-BHP is readily soluble in the reaction mixture and is less hydrophilic than H_2O_2 . Furthermore, the amount of water in the 70% *t*-BHP solution is less than that in the 30% H_2O_2 solution.

4. Conclusions

The main product of the oxidation of *cis*-pinane **1** with *t*-BHP over copper, cobalt, iron and manganese phthalocyanines encapsulated in

Y zeolites, at room temperature and atmospheric pressure, is 2-pinane hydroperoxide **2**.

Products of the oxidation of **1** on C3 and C4, like pinocampheol **3**, verbanol **4** and the corresponding ketones, as well as 2-pinanol **5** are mainly formed in homogeneous phase in the case of FePc and MnPc. Free MPc complexes yield both **2** and **5**, depending the ratio of **2/5** on the amount of complex. This means that **2** is in both cases the primary oxidation product, being the reaction initiated by the decomposition of *t*-BHP that proceeds by a chain radical mechanism. The formation of **5** results from the decomposition of pinane hydroperoxide by the MPc complexes. With the MPcNaY catalysts, **2** is not decomposed because, by sterical reasons, it cannot approach the metal centre.

The experiments carried out with slow addition of *t*-BHP (semibatch conditions) give yields of **2** even higher than those observed when batch conditions are carried out. Such results are most likely due to the lipophilic/hydrophilic balance within the zeolite pores. Under semibatch conditions, this balance is decreasing with the course of the reaction, becoming more and more difficult the diffusion of pinane into the zeolite. Using these assumptions, a kinetic model was built that reasonably fits experimental data.

The catalytic activity depends also on the oxygen donor, having been observed the order $t\text{-BuOOH} \gg \text{O}_2 > \text{H}_2\text{O}_2$.

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